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(57) Abstract

A mixture of at least one thermal carbene-free ruthenium catalyst A and at least one thermal ruthenium carbene catalyst B, both of which initiate the ring-opening metathesis polymerisation on their own, said catalysts being present in a weight ratio of A to B from 10:1 to 1:10. By adding this mixture even in small amounts, the ring-opening metathesis polymerisation of strained cycloolefins can be effectively catalysed.

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Catalyst mixture and polymerisable composition.

The present invention relates to a mixture consisting of at least one thermal ruthenium catalyst A and at least one ruthenium carbene catalyst B, both of which initiate the ring-opening metathesis polymerisation on their own, said catalysts being present in a weight ratio of A to B from10 :1 to 1:10; to a composition consisting of at least one strained cycloolefin and a catalytically effective amount of the ruthenium catalyst mixture; to a process for the polymerisation of strained cycloolefins; to shaped articles of polymers of said composition and to the use of the ruthenium catalyst mixture for the ring-opening metathesis polymerisation of strained cycloolefins.

The ring-opening metathesis polymerisation of strained cycloolefins such as norbornene with catalysts selected from the ruthenium compound group is known and has been repeatedly described in the literature.

A. Demonceau et al. in J. Mol. Catal. 76:123-132 (1992), for example, describe ruthenium compounds as suitable metathesis polymerisation catalysts of e.g. norbornene, where the reactivity can be increased by the addition of diazo esters.

In Tetrahedron Letters 52:4589-4592 (1977), C. Tanelian et al. report that the ruthenium compound $RuCl_2[P(C_6H_5)_3]_3$ is a suitable catalyst for the metathesis polymerisation but that it is deactivated by dicyclopentadiene and then no polymers are formed.

WO 93/20111 proposes the use of ruthenium compounds with phosphine ligands, for example $[(H_5C_6)_3P]_2Cl_2Ru{=}CH{-}CH{=}C(C_6H_5)_2$, as thermal catalysts for the ring-opening metathesis polymerisation of strained cycloolefins, where cyclodienes such as dicyclopentadiene act as catalyst inhibitors and therefore cannot be polymerised. These "metal carbenes" are sparingly soluble compounds, so that the polymerisations are only possible in polar and, where appropriate, protic solutions. The same catalysts are described by S. Kanaoka in Macromolecules 1995, 28, pages 4707 to 4713 under the same conditions of solution polymerisation for the preparation of copolymers with silicon-containing norbornene derivatives.

In Polym. Prepr. 1995, 36, pages 237 to 238, C. Fraser et al. describe ruthenium carbenes having a $Ru{=}CH{-}C_6H_5$ group which are effective catalysts for the metathesis polymerisation. A substantial disadvantage of these catalysts is their high reactivity which makes it necessary to process polymerisable compositions directly after the components are mixed.

WO 95/07310 describes a ring-opening photopolymerisation of strained cycloolefins under the action of ruthenium compounds with photolabile ligands as catalysts. After being irradiated, these catalysts can also be used as thermal catalysts.

Carbene-free ruthenium catalysts normally must be used in amounts of more than 0.3 % by weight, and ruthenium carbene catalysts normally must be used in amounts of more than 0.1 % by weight, based on the cycloolefin, in order to obtain, within reasonable polymerisation times, well polymerised shaped artices having good mechanical and physical properties. If lower amounts are used, the polymerisation is not complete anymore which can be detected by the inherent smell of the monomers used and their bad physical and mechanical properties. It is not possible to prepare useful shaped articles using such low amounts.

The ruthenium catalysts are expensive and their use in higher amounts as catalysts is uneconomical. Another disadvantage is that the use of high amounts of catalysts also leads to high amounts of ruthenium residues in the polymers, which is undesirable for toxic reasons, adversely affects the stability of the polymer and must be avoided in particular where there is contact with electrical or electronic components.

Surprisingly, it has now been found that the high reactivity of the ruthenium carbene catalysts can be reduced, a latency of polymerisable compositions can be achieved and, within a specific scope, even the reactivity can be adjusted, which obviates immediate processing owing to the improved storage stability achieved, if mixtures consisting of carbene-free (a) ruthenium catalysts and (b) ruthenium carbene catalysts are used. It has also, surprisingly, been found that despite their latency, the catalyst mixtures have very high reactivity and that therefore the mixture can be used in substantially lower, and accordingly in more economic, amounts than the individual components, still giving polymers having comparable physical and mechanical properties. Furthermore, the metal content in the polymers can be reduced in this manner, which enhances the properties of the polymer and which also permits applications in contact with electrical or electronic components. The described effects

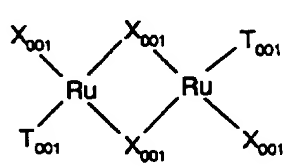
are particularly pronounced when mixtures consisting of carbene-free (a) ruthenium catalysts with phosphine ligands substituted by sterically demanding hydrocarbon radicals, and with (b) ruthenium carbene catalysts are used. It has also been found that ruthenium compounds which do not initiate the polymerisation when used in high amounts of e.g. 0.5 % by weight, result in useful shaped articles if they are added in smaller amounts in admixture with ruthenium carbene catalysts.

In one of its aspects, this invention relates to a mixture of at least one thermal carbene-free ruthenium catalyst A and at least one thermal ruthenium carbene catalyst B, both of which initiate the ring-opening metathesis polymerisation on their own, said catalysts being present in a weight ratio of A to B from 10:1 to 1:10.

Within the scope of this invention, thermal signifies that the ring-opening metathesis polymerisation is initiated by the catalysts under the action of heat.

The weight ratio of A to B is preferably from 8:1 to 1:2, more preferably from 6:1 to 1:1, particularly preferably from 5:1 to 1:1 and, most preferably, from 3:1 to 1:1.

The carbene-free ruthenium catalysts A may be compounds having one (mononuclear) or two (binucluear) ruthenium atoms. The binuclear ruthenium compounds may typically be those of formula XI



(XI),

wherein X_{001} is Cl, Br or I, preferably Cl, and T_{001} is unsubstituted or C_1-C_6alkyl-substituted C_6-C_{18}arene or C_4-C_{17}heteroarene.

Arene preferably contains 6 to 12 carbon atoms and heteroarene preferably contains 4 to 10 carbon atoms and 1 or 2 hetero atoms selected from the group consisting of O, N and S in one or several rings. Arene and heteroarene can be monocyclic or condensed rings. Typical examples of alkyl substituents are methyl, ethyl, n- and i-propyl, n-, i- and t-butyl.

Typical examples of arenes are benzene, toluene, xylene, cumene, naphthalene, anthracene, naphthacene, chrysene and biphenyl. Typical examples of heteroarene are furan, thiophene, benzofuran, benzothiophene, pyrrole and pyridine.

Of the thermal ruthenium catalysts, those are particularly suitable and preferred that contain phosphine ligands. Particularly preferred are divalent-cationic ruthenium compounds containing at least one phosphine group and a total of 2 to 5 ligands bonded to the ruthenium atom and which contain acid anions for charge equalisation.

In the ruthenium compounds for use according to this invention a monophosphine can be bound to the metal atom once, twice or three times, and a diphosphine can be bound to the metal atom once. In these ruthenium catalysts a total of preferably 1 to 4, more preferably 1 to 3 and, particularly preferably, 2 ligands are bonded. The phosphine ligands preferably conform to formulae VII and VIIa

$$PR_{26}R_{27}R_{28} \quad \text{(VII)},$$

$$R_{26}R_{27}P\text{-}Z_1\text{-}PR_{26}R_{27} \quad \text{(VIIa)},$$

wherein R_{26}, R_{27} and R_{28} are each independently of one another H, C_1-C_{20}alkyl, C_1-C_{20}-alkoxy; C_4-C_{12}cycloalkyl or cycloalkoxy which is unsubstituted or substituted by C_1-C_6alkyl, C_1-C_6haloalkyl or C_1-C_6alkoxy, or C_6-C_{16}aryl or C_6-C_{16}aryloxy which is unsubstituted or substituted by C_1-C_6alkyl, C_1-C_6haloalkyl or C_1-C_6alkoxy, or C_7-C_{16}aralkyl or C_7-C_{16}aralkyloxy which is unsubstituted or substituted by C_1-C_6alkyl, C_1-C_6haloalkyl or C_1-C_6alkoxy; R_{26} and R_{27} together are tetra- or pentamethylene or tetra- or pentamethylenedioxyl, each of which is unsubstituted or substituted by C_1-C_6-alkyl, C_1-C_6haloalkyl or C_1-C_6alkoxy, or tetra- or pentamethylene or tetra- or pentamethylenedioxyl, each of which is unsubstituted or substituted by C_1-C_6alkyl, C_1-C_6haloalkyl or C_1-C_6-alkoxy and condensed with 1 or 2 1,2-phenylene, or tetramethylenedioxyl which is unsubstituted or substituted by C_1-C_6alkyl, C_1-C_6haloalkyl or C_1-C_6alkoxy and condensed in the 1,2- and 3,4-positions with 1,2-phenylene, and R_{28} is as defined above; and
Z_1 is linear or branched, unsubstituted or C_1-C_4alkoxy-substituted C_2-C_{12}alkylene, unsubstituted or C_1-C_4alkyl- or C_1-C_4alkoxy-substituted 1,2- or 1,3-cycloalkylene of 4 to 8 carbon

atoms, or unsubstituted or C_1-C_4alkyl- or C_1-C_4alkoxy-substituted 1,2- or 1,3-heterocycloalkylene having 5 or 6 ring members and a hetero atom selected from the O or N group.

R_{26}, R_{27} and R_{28} are preferably identical. Particularly preferred are also sterically demanding radicals, typically branched, preferably α-branched alkyl, or cyclic radicals. Hydrocarbon radicals are also particularly preferred. Preferred phoshines are those of formula VII, which are tertiary phosphines, and diphosphines of formula VIIa, which are ditertiary diphosphines.

R_{26}, R_{27} and R_{28} defined as alkyl may be linear or branched and may contain preferably 1 to 12, more preferably 1 to 8 and, particularly preferably, 1 to 6 carbon atoms. Illustrative examples of alkyl are methyl, ethyl, n- and i-propyl, n-, i- and t-butyl, the isomers of pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl and eicosyl. Preferred examples are methyl, ethyl, n- and i-propyl, n-, i- and t-butyl, 1-, 2- or 3-pentyl and 1-, 2-, 3- or 4-hexyl.

If R_{26}, R_{27} and R_{28} are substituted, the substituents are preferably C_1-C_4alkyl, C_1-C_4haloalkyl or C_1-C_4alkoxy. Halogen is preferably Cl and, particularly preferably, F. Typical examples of preferred substituents are methyl, methoxy, ethyl, ethoxy and trifluoromethyl. R_{26}, R_{27} and R_{28} are preferably substituted one to three times.

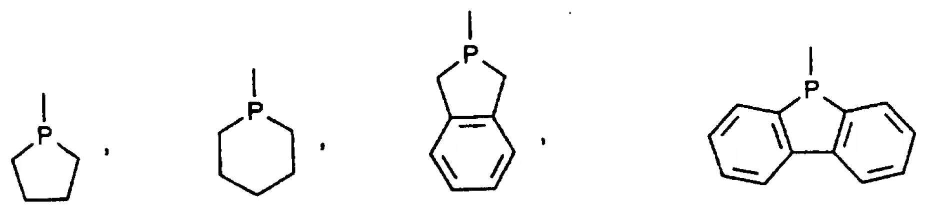
R_{26}, R_{27} and R_{28} defined as cycloalkyl are preferably C_5-C_8cycloalkyl and, particularly preferably, C_5- or C_6cycloalkyl. Some examples are cyclobutyl, cycloheptyl, cyclooctyl and, preferably, cyclopentyl and cyclohexyl. Typical examples of substituted cycloalkyl are methyl-, dimethyl-, trimethyl-, methoxy-, dimethoxy-, trimethoxy-, trifluoromethyl-, bistrifluoromethyl and tristrifluoromethylcyclopentyl and -cyclohexyl.

R_{26}, R_{27} and R_{28} defined as aryl are preferably C_6-C_{12}aryl and, particularly preferably, phenyl or naphthyl. Typical examples of substituted aryl are methyl-, dimethyl-, trimethyl-, methoxy-, dimethoxy-, trimethoxy-, trifluoromethyl-, bistrifluoromethyl- and tristrifluoromethylphenyl.

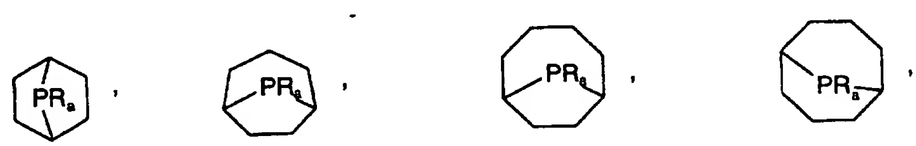
R_{26}, R_{27} and R_{28} defined as aralkyl are preferably C_7-C_{13}aralkyl, the alkylene group in aralkyl preferably being methylene. Aralkyl is particularly preferably benzyl. Illustrative examples of

substituted aralkyl are methyl-, dimethyl-, trimethyl-, methoxy-, dimethoxy-, trimethoxy-, trifluoromethyl-, bistrifluoromethyl- and tristrifluoromethylbenzyl.

Illustrative examples of tetra- and pentamethylene which are bonded to the P atom and which are unsubstituted or substituted or condensed, are



Other suitable phosphines are cycloaliphates which are brigded with a $=PR_a$ group containing 6 to 8 ring carbon atoms, for example



wherein R_a is C_1-C_{20}alkyl, preferably C_1-C_{12}alkyl, particularly preferably C_1-C_6alkyl, cyclohexyl, benzyl, or phenyl which is unsubstituted or substituted by 1 or 2 C_1-C_4alkyl.

Z_1 defined as linear or branched alkylene is preferably 1,2-alkylene or 1,3-alkylene of preferably 2 to 6 carbon atoms, typically ethylene, 1,2-propylene or 1,2-butylene.

Typical examples of Z_1 defined as cycloalkylene are 1,2- and 1,3-cyclopentylene, and 1,2- or 1,3-cyclohexylene. Typical examples of Z_1 defined as heterocycloalkylene are 1,2- and 1,3-pyrrolidine, 1,2- and 1,3-piperidine, and 1,2- and 1,3-tetrahydrofuran.

In a preferred embodiment of this invention, the phosphine ligands conform to formula VII, wherein R_{26}, R_{27} and R_{28} are each independently of one another H, C_1-C_6alkyl, unsubstituted or C_1-C_4alkyl-substituted cyclopentyl or cyclohexyl, or phenyl which is unsubstituted or substituted by C_1-C_4alkyl, C_1-C_4alkoxy or trifluoromethyl, or benzyl which is unsubstituted or

substituted by C_1-C_4alkyl, C_1-C_4alkoxy or trifluoromethyl. Particularly preferred examples of phosphine ligands of formula VII are
$(C_6H_5)H_2P$, $(3\text{-}CH_3\text{-}6\text{-}t\text{-}C_4H_9\text{-}C_6H_3)_3P$, $(3\text{-}CH_3\text{-}6\text{-}t\text{-}C_4H_9\text{-}C_6H_3)_3P$, PH_3, $(2,6\text{-Di-}t\text{-}C_4H_9\text{-}C_6H_3)_3P$, $(2,3\text{-Di-}t\text{-}C_4H_9\text{-}C_6H_3)_3P$, $(2,4\text{-Di-}t\text{-}C_4H_9\text{-}C_6H_3)_3P$, $(2,4\text{-Di-}CH_3\text{-}C_6H_3)_3P$, $(2,6\text{-Di-}CH_3\text{-}C_6H_3)_3P$, $(2\text{-}CH_3\text{-}6\text{-}t\text{-}C_4H_9\text{-}C_6H_3)_3P$, $(CH_3)_3P$, $(2\text{-}i\text{-}C_3H_7\text{-}C_6H_4)_3P$, $(3\text{-}i\text{-}C_3H_7\text{-}C_6H_4)_3P$, $(4\text{-}i\text{-}C_3H_7\text{-}C_6H_4)_3P$, $(2\text{-}n\text{-}C_4H_9\text{-}C_6H_4)_3P$, $(3\text{-}n\text{-}C_4H_9\text{-}C_6H_4)_3P$, $(4\text{-}n\text{-}C_4H_9\text{-}C_6H_4)_3P$, $(2\text{-}i\text{-}C_4H_9\text{-}C_6H_4)_3P$, $(3\text{-}i\text{-}C_4H_9\text{-}C_6H_4)_3P$, $(4\text{-}i\text{-}C_4H_9\text{-}C_6H_4)_3P$, $(2\text{-}t\text{-}C_4H_9\text{-}C_6H_4)_3P$, $(3\text{-}t\text{-}C_4H_9\text{-}C_6H_4)_3P$, $(4\text{-}t\text{-}C_4H_9\text{-}C_6H_4)_3P$, $(4\text{-}C_2H_5\text{-}C_6H_4)_3P$, $(3\text{-}n\text{-}C_3H_7\text{-}C_6H_4)_3P$, $(2\text{-}n\text{-}C_3H_7\text{-}C_6H_4)_3P$, $(4\text{-}n\text{-}C_3H_7\text{-}C_6H_4)_3P$, $(C_2H_5)_2HP$, $(3\text{-}CH_3\text{-}C_6H_4)_3P$, $(4\text{-}CH_3\text{-}C_6H_4)_3P$, $(2\text{-}C_2H_5\text{-}C_6H_4)_3P$, $(3\text{-}C_2H_5\text{-}C_6H_4)_3P$, $(i\text{-}C_3H_7)H_2P$, $(n\text{-}C_4H_9)H_2P$, $(C_6H_5CH_2)_2HP$, $(C_6H_5CH_2)H_2P$, $(2\text{-}CH_3\text{-}C_6H_4)_3P$, $(C_6H_6)_3P$, $(C_5H_{11})H_2P$, $(C_6H_5CH_2)_3P$, $(n\text{-}C_3H_7)_2HP$, $(i\text{-}C_3H_7)_2HP$, $(n\text{-}C_4H_9)_2HP$, $(n\text{-}C_3H_7)H_2P$, $(C_2H_5)H_2P$, $(C_5H_{11})_3P$, $(C_6H_5)_2HP$, $(C_5H_{11})_2HP$, $(n\text{-}C_3H_7)_3P$, $(i\text{-}C_3H_7)_3P$, $(n\text{-}C_4H_9)_3P$, $(CH_3)_2HP$, $(C_2H_5)_3P$, $(C_6H_{11})_3P$, $(C_6H_{11})_2HP$, $(C_5H_9)_3P$, $(C_5H_9)_2HP$ and $(CH_3)H_2P$.

Particularly preferred phosphines are triphenylphosphine, tri-i-propylphosphine, tri-t-butylphosphine, tricyclopentylphosphine and tricyclohexylphosphine.

Ligands for the ruthenium compounds to be used according to this invention are organic or inorganic compounds, atoms or ions which are coordinated to a metal centre.

Within the scope of this invention, it is particularly convenient to use those ligands which are selected from a group of ligands (A) consisting of nitrogen (N_2); monocyclic, polycyclic or condensed arenes which are unsubstituted or substituted by OH, C_1-C_4alkyl, C_1-C_4alkoxy, C_6-C_{12}aryl or halogen and containing 6 to 24, preferably 6 to 18 and, particularly preferably, 6 to 12, carbon atoms; monocyclic heteroarenes which are unsubstituted or substituted by C_1-C_4alkyl, C_1-C_4alkoxy or halogen; condensed heteroarenes; condensed arene/ heteroarenes containing 3 to 22, preferably 4 to 16 and, particularly preferably, 4 to 10, carbon atoms, and 1 to 3 hetero atoms selected from the group consisting of O, S and N; and aliphatic, cycloaliphatic, aromatic or araliphatic nitriles which are unsubstituted or substituted by C_1-C_4alkyl, C_1-C_4alkoxy or halogen and containing 1 to 22, preferably 1 to 18, particularly preferably 1 to 12 and, very particularly preferably, 1 to 7, carbon atoms. The preferred substituents are methyl, ethyl, methoxy, ethoxy, fluoro, chloro and bromo. The arenes and

heteroarenes are preferably substituted by one to three radicals. Of the heteroarenes the electron-rich heteroarenes are preferred.

Some examples of arenes and heteroarenes are benzene, cumene, biphenyl, naphthalene, anthracene, acenaphthene, fluorene, phenanthrene, pyrene, chrysene, fluoroanthrene, furan, thiophene, pyrrole, pyridine, γ-pyran, γ-thiopyran, pyrimidine, pyrazine, indole, coumarone, thionaphthene, carbazole, dibenzofuran, dibenzothiophene, pyrazole, imidazole, benzimidazole, oxazole, thiazole, isoxazole, isothiazole, quinoline, isoquinoline, acridine, chromene, phenazine, phenoxazine, phenothiazine, triazines, thianthrene and purine. Preferred arenes and heteroarenes are unsubstituted or substituted benzene, naphthalene, cumene, thiophene and benzothiophene. Arene is very particularly preferably benzene or benzene which is substituted by 1 to 3 C_1-C_4alkyl such as toluene, xylene, trimethylbenzene, isopropylbenzene, tertiary butylbenzene or cumene. Heteroarene is preferably thiophene.

The nitriles may typically be substituted by methoxy, ethoxy, fluoro or chloro. The nitriles are preferably unsubstituted. The alkyl nitriles are preferably linear. Some examples of nitriles are acetonitrile, propionitrile, butyronitrile, pentylnitrile, hexylnitrile, cyclopentylnitrile and cyclohexylnitrile, benzonitrile, methylbenzonitrile, benzyl nitrile and naphthyl nitrile.The nitriles are preferably linear C_1-C_4alkylnitriles or benzonitrile. Of the alkylnitriles, acetonitrile is particularly preferred.

In a preferred subgroup, the ligands of the group (A) are N_2, benzene, thiophene, benzonitrile or acetonitrile which are unsubstituted or substituted by one to three C_1-C_4alkyl.

Where appropriate, further ligands are present, for examples those selected from the ligand group (B) consisting of solvating inorganic and organic compounds containing the hetero atoms O, S or N, which are also often used as solvents; and cyclopentadienyl or indenyl which are unsubstituted or substituted by C_1-C_4alkyl, C_1-C_4alkoxy, $(C_1$-$C_4alkyl)_3Si$ or $(C_1$-$C_4alkyl)_3SiO$-. Typical examples of such compounds are H_2O, H_2S, NH_3; unsubstituted or halogenated, preferably fluorinated or chlorinated, aliphatic or cycloaliphatic alcohols or mercaptans containing 1 to 18, preferably 1 to 12 and, particularly preferably, 1 to 6, carbon atoms, aromatic alcohols or thiols containing 6 to 18, preferably 6 to 12, carbon atoms, araliphatic alcohols or thiols containing 7 to 18, preferably 7 to 12, carbon atoms; open-

chain or cyclic and aliphatic, araliphatic or aromatic ethers, thioethers, sulfoxides, sulfones, ketones, aldehydes, carboxylates, lactones, carboxamides which may be N-C_1-C_4mono- or -dialkylated and containing 2 to 20, preferably 2 to 12 and, particularly preferably, 2 to 6, carbon atoms, and lactams which may be N-C_1-C_4alkylated; open-chain or cyclic and aliphatic, araliphatic or aromatic, primary, secondary and tertiary amines containing 1 to 20, preferably 1 to 12 and, particularly preferably, 1 to 6, carbon atoms; and cyclopentadienyls such as cyclopentadienyl, indenyl; cyclopentadienyls or indenyls which are methylised or trimethylsilylated once or several times. Typical examples also include allyl, metallyl and crotyl.

Further examples of the ligands of group (B) are methanol, ethanol, n- and i-propanol, n-, i- and t-butanol, 1,1,1-trifluoroethanol, bistrifluoromethylmethanol, tristrifluoromethylmethanol, pentanol, hexanol, methylmercaptan or ethylmercaptan, cyclopentanol, cyclohexanol, cyclohexylmercaptan, phenol, methylphenol, fluorophenol, phenylmercaptan, benzylmercaptan, benzyl alcohol, diethyl ether, dimethyl ether, diisopropyl ether, di-n-butyl ether or di-t-butyl ether, tetrahydrofuran, tetrahydropyrane, dioxane, diethyl sulfide, tetrahydrothiophene, dimethylsulfoxide, diethylsulfoxide, tetra- and pentamethylenesulfoxide, dimethyl sulfone, diethyl sulfone, tetra- and pentamethylenesulfone, acetone, methyl ethyl ketone, diethyl ketone, phenylmethyl ketone, methylisobutyl ketone, benzylmethyl ketone, acetaldehyde, propionaldehyde, trifluoroacetaldehyde, benzaldehyde, ethyl acetate, butyrolactone, dimethylformamide, dimethylacetamide, pyrrolidone and N-methylpyrrolidone, indenyl, cyclopentadienyl, methyl- or dimethyl- or pentamethylcyclopentadienyl, and trimethylsilylcyclopentadienyl.

The primary amines may conform to formula $R_{29}NH_2$, the secondary amines to formula $R_{29}R_{30}NH$ and the tertiary amines to formula $R_{29}R_{30}R_{31}N$, wherein R_{29} is C_1-C_{18}alkyl, unsubstituted or C_1-C_4alkyl- or C_1-C_4alkoxy-substituted C_5- or C_6cycloalkyl, or unsubstituted or C_1-C_4alkyl- or C_1-C_4alkoxy-substituted C_6-C_{18}aryl or C_7-C_{12}aralkyl, R_{30} independently has the meaning of R_{29}, or R_{29} and R_{30} together are tetramethylene, pentamethylene, 3-oxa-1,5-pentylene or $-CH_2-CH_2-NH-CH_2-CH_2-$ or $-CH_2-CH_2-N(C_1\text{-}C_4\text{alkyl})-CH_2-CH_2-$, and R_{31} independently has the meaning of R_{29}. Alkyl preferably contains 1 to 12 and, particularly preferably, 1 to 6, carbon atoms. Aryl preferably contains 6 to 12 carbon atoms, and aralkyl preferably contains 7 to 9 carbon atoms. Typical examples of amines are methyl-, dimethyl-, trimethyl-, ethyl-, diethyl-, triethyl-, methylethyl-, dimethylethyl, n-propyl-, di-n-propyl-, tri-n-

butyl-, cyclohexyl-, phenyl- and benzylamine, as well as pyrrolidine, N-methylpyrrolidine, piperidine, piperazine, morpholine and N-methylmorpholine.

In a preferred subgroup, the ligands of group (B) are H_2O, NH_3, unsubstituted or partially or completely fluorinated C_1-C_4alkanols, or cyclopentadienyl, indenyl, allyl, metallyl or crotyl. H_2O, NH_3, cyclopentadienyl, indenyl, methanol and ethanol are very particularly preferred.

In a preferred embodiment of this invention, the Ru catalysts and Os catalysts to be used according to this invention contain arenes or heteroarenes as ligands, phosphine groups and anions for charge equalisation. Very particularly preferably they contain an arene group as ligand, a tertiary phosphine group and mono- or divalent anions for charge equalisation.

Suitable anions of inorganic or organic acids are, for example, hydride (H^-), halide (e.g. F^-, Cl^-, Br^- and I^-), the anion of an oxygen acid, and BF_4^-, PF_6^-, SbF_6^- or AsF_6^-. It may be mentioned that the above ligands cyclopentadienyl, indenyl, allyl, metallyl and crotyl are anionic and thus also serve the charge equalisation.

Futher suitable anions are C_1-C_{12}alcoholates, preferably C_1-C_6alcoholates and, particularly preferably, C_1-C_4alcoholates, which are preferably branched and which typically conform to formula $R_xR_yR_zC$-O^-, wherein R_x is H or C_1-C_{10}alkyl, R_y is C_1-C_{10}alkyl, and R_z is C_1-C_{10}alkyl or phenyl, the sum of the carbon atoms of R_x, R_y and R_z being at least 2, preferably at least 3 and up to 10. Examples include in particular i-propyloxy and t-butyloxy.

Further suitable anions are C_3-C_{18}acetylides, preferably C_5-C_{14}acetylides and, particularly preferably, C_5-C_{12}acetylides, which may conform to formula R_w-$C{\equiv}C^-$, wherein R_w is C_1-C_{16}-alkyl, preferably α-branched C_3-C_{12}alkyl, typically formula $R_xR_yR_zC$-, or phenyl or benzyl which are unsubstituted or substituted by 1 to 3 C_1-C_4alkyl or C_1-C_4alkoxy. Some examples are i-propyl-, i- and t-butyl-, phenyl-, benzyl-, 2-methyl-, 2,6-dimethyl-, 2-i-propyl-, 2-i-propyl-6-methyl-, 2-t-butyl-, 2,6-di-t-butyl- and 2-methyl-6-t-butylphenylacetylide.

The anions of oxygen acids can be, for example, sulfate, phosphate, perchlorate, perbromate, periodate, antimonate, arsenate, nitrate, carbonate, the anion of a C_1-C_8-carbonic acid such as formiate, acetate, propionate, butyrate, benzoate, phenylacetate, mono-, di- or tri-

chloroacteate or mono-, di- or trifluoroacetate, sulfonates such as methylsulfonate, ethylsulfonate, propylsulfonate, butylsulfonate, trifluoromethylsulfonate (triflat); phenylsulfonate or benzylsulfonate which is unsubstituted or substituted by C_1-C_4alkyl, C_1-C_4alkoxy or halogen, preferably fluoro, chloro or bromo, typically tosylate, mesylate, brosylate, p-methoxy- or p-ethoxyphenylsulfonate, pentafluorophenylsulfonate or 2,4,6-triisopropylsulfonate, and phosphonates such as methylphosphonate, ethylphosphonate, propylphosphonate, butylphosphonate, phenylphosphonate, p-methylphenylphosphonate or benzylphosphonate.

Particularly preferred are H^-, F^-, Cl^-, Br^-, BF_4^-, PF_6^-, SbF_6^-, AsF_6^-, $CF_3SO_3^-$, C_6H_5-SO_3^-, 4-methyl-C_6H_5-SO_3^-, 3,5-dimethyl-C_6H_5-SO_3^-, 2,4,6-trimethyl-C_6H_5-SO_3^- and 4-CF_3-C_6H_5-SO_3^- as well as cyclopentadienyl (Cp^-).

In a preferred embodiment of this invention, the ruthenium compounds conform to one of formulae VIII to VIIId

$$R_{32}L_1Me^{2+}(Z^{n-})_{2/n} \qquad \text{(VIII)},$$

$$R_{32}L_1L_2Me^{2+}(Z^{n-})_{2/n} \qquad \text{(VIIIa)},$$

$$(R_{32})_2L_1Me^{2+}(Z^{n-})_{2/n} \qquad \text{(VIIIb)},$$

$$(R_{32})_3L_1Me^{2+}(Z^{n-})_{2/n} \qquad \text{(VIIIc)},$$

$$R_{32}(L_1)_2Me^{2+}(Z^{n-})_{2/n} \qquad \text{(VIIId)},$$

wherein
R_{32} is a phosphine ligand of formula VII or VIIa;
Me is Ru;
n is 1, 2 or 3;
Z is the anion of an inorganic or organic acid;
(a) L_1 is a ligand of group A, L_1 in formula VIIId being identical or different, and
(b) L_2 is a ligand of group B.

R_{32}, Z, L_1 and L_2 have the meanings and preferred meanings cited above for the phosphines of formulae VII and VIIa.

In formulae VIII to VIIId, n is preferably 1 or 2 and, particularly preferably, 1. R_{32} has the preferred meanings cited for the phosphine ligands of formulae VII and VIIa; they are preferably tertiary phosphines.

It is very particularly preferred to use ruthenium compounds of one of formulae IX to IXd

$(R_{26}R_{27}R_{28}P)L_1Me^{2+}(Z_1^{1-})Z_2^{-1}$ (IX),

$(R_{26}R_{27}R_{28}P)_2L_1Me^{2+}(Z_1^{1-})Z_2^{-1}$ (IXa),

$(R_{26}R_{27}R_{28}P)L_1L_2Me^{2+}(Z_1^{1-})Z_2^{-1}$ (IXb),

$(R_{26}R_{27}R_{28}P)_3L_1Me^{2+}(Z_1^{1-})Z_2^{-1}$ (IXc),

$(R_{26}R_{27}R_{28}P)(L_1)_2Me^{2+}(Z_1^{1-})Z_2^{-1}$ (IXd),

wherein

Me is Ru;

Z_1 and Z_2 are each independently of the other H^-, cyclopentadienyl, Cl^-, Br^-, BF_4^-, PF_6^-, SbF_6^-, AsF_6^-, $CF_3SO_3^-$, C_6H_5-SO_3^-, 4-methyl-C_6H_5-SO_3^-, 3,5-dimethyl-C_6H_5-SO_3^-, 2,4,6-trimethyl-C_6H_5-SO_3^- or 4-CF_3-C_6H_5-SO_3^-;

R_{26}, R_{27} and R_{28} are each independently of one another C_1-C_6alkyl, or cyclopentyl or cyclohexyl or cyclopentyloxy or cyclohexyloxy, each of which is unsubstituted or substituted by 1 to 3 C_1-C_4alkyl, or phenyl or benzyl or phenyloxy or benzyloxy, each of which is unsubstituted or substituted by 1 to 3 C_1-C_4alkyl;

L_1 is C_6-C_{16}arene or C_5-C_{16}heteroarene which is unsubstituted or substituted by 1 to 3 C_1-C_4alkyl, C_1-C_4alkoxy, -OH, -F or Cl, or C_1-C_6alkyl-CN, benzonitrile or benzylnitrile, L_1 in formula IXd being identical or different; and

L_2 is H_2O or C_1-C_6alkanol.

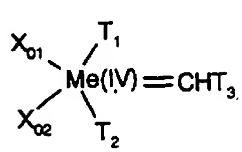
If the preparation of the ruthenium catalysts is carried out in solvents which can coordinate to a metal atom, such as to alkanols, then solvating Ru cation complexes can form which are included within the scope of the use of the novel compositions.

Some examples of ruthenium compounds to be used according to this invention are: [tos signifies tosylate]: $(C_6H_{11})_2HPRu$(p-cumene)Cl_2, $(C_6H_{11})_3PRu$(p-cumene)Cl_2, $(C_6H_{11})_3PRu$(p-cumene)$(tos)_2$, $(C_6H_{11})_3PRu$(p-cumene)Br_2, $(C_6H_{11})_3PRu$(p-cumene)ClF, $(C_6H_{11})_3PRu(C_6H_6)$-$(tos)_2$, $(C_6H_{11})_3PRu(CH_3$-$C_6H_5)(tos)_2$, $(C_6H_{11})_3PRu(C_{10}H_8)(tos)_2$, (i-$C_3H_7)_3PRu$(p-cumene)$Cl_2$, $(CH_3)_3PRu$(p-cumene)Cl_2, $(C_6H_{11})_3PRu(CH_3$-CN)$(C_2H_5$-OH)$(tos)_2$, $(C_6H_{11})_3PRu$(p-cumene)-$(CH_3$-$CN)_2(PF_6)_2$, $(C_6H_{11})_3PRu$(p-cumene)$(CH_3$-$CN)_2(tos)_2$, (n-$C_4H_9)_3PRu$(p-cumene)$(CH_3$-$CN)_2(tos)_2$, $(C_6H_{11})_3PRu(CH_3CN)Cl_2$, $(C_6H_{11})_3PRu(CH_3$-$CN)_2Cl_2$, (n-$C_4H_9)_3PRu$(p-cumene)Cl_2, $(C_6H_{11})_3PRu$(p-cumene)$(C_2H_5OH)_2(BF_4)_2$, $(C_6H_{11})_3PRu$(p-cumene)$(C_2H_5OH)_2(PF_6)_2$, $[(C_6H_{11})_3P]_3Ru(CH_3$-CN), $(C_5H_9)_3PRu$(p-cumene)Cl_2, $(C_6H_{11})_3PRu$(p-cumene)HCl, $(C_6H_{11})_3PRu[1,2,4,5$-$(CH_3)_4C6H_2]Cl_2$, $(C_6H_{11})_3PRu[1,3,5$-(i-$C_3H_7)_3C_6H_3]Cl_2$, $(C_6H_{11})_3PRu$-$[(C_4H_9)$-$C_6H_5]Cl_2$, $(C_6H_5)_3PRu$(p-cumene)HCl, $[(C_6H_{11})_3P]_2Ru(CH_3$-CN)$(tos)_2$, $RuCl_2$(p-cumene)$[(C_6H_{11})_2PCH_2CH_2P(C_6H_{11})_2]$, $(C_6H_{11})_3PRu$(p-cumene)$(C_2H_5OH)(BF_4)_2$, $(C_6H_{11})_3PRu$-$(C_6H_6)(C_2H_5OH)_2(tos)_2$, $(C_6H_{11})_3PRu$(i-C_3H_7-$C_6H_5)(tos)_2$, $(C_6H_{11})_3PRu(C_6H_6)$(p-cumene)Br_2, $(C_6H_{11})_3PRu$(biphenyl)$(tos)_2$, $(C_6H_{11})_3PRu$(anthracene)$(tos)_2$, (2-$CH_3C_6H_4)_3PRu$(p-cumene)Cl_2 and $(C_6H_{11})_3PRu$(chrysene)$(tos)_2$.

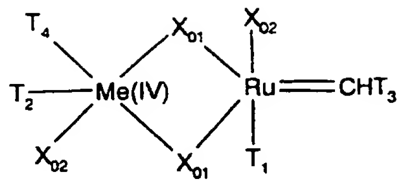
These ruthenium compounds to be used according to this invention are known or can be prepared by known and analogous methods starting from the metal halides (for example RuX_3 or $[RuareneX_2]_2$ and by reaction with phosphines and ligand formers.

The thermal ruthenium carbene catalysts B are preferably ruthenium carbene having two phosphine ligands and two halogen atoms.

Said ruthenium carbene catalysts B may preferably conform to formula X or Xa or to mixtures of compounds of formulae X and Xa



(X),



(Xa),

wherein

Me is ruthenium;

T_1 and T_2 are each independently of the other a tertiary phosphine, or T_1 and T_2 together are a ditertiary diphosphine;

T_3 is H, C_1-C_{12}alkyl; C_3-C_8cycloalkyl, C_3-C_7heterocycloalkyl having one or two hetero atoms selected from the group consisting of -O-, -S- and -N-, C_6-C_{14}aryl, or C_4-C_{15}heteroaryl having one to three hetero atoms selected from the group consisting of -O-, -S- and -N- , which are unsubstituted or substituted by C_1-C_{12}alkyl, C_1-C_{12}haloalkyl, C_1-C_{12}alkoxy, C_6-C_{10}aryl, C_6-C_{10}-aryloxy -NO_2 or halogen;

T_4 is C_6-C_{16}arene or C_4-C_{15}heteroarene which is unsubstituted or substituted by 1 to 3 C_1-C_4-alkyl, C_1-C_4haloalkyl, C_1-C_4alkoxy, -OH, F, Cl or Br, and

X_{01} and X_{02} are each independently of the other halogen.

X_{01} and X_{02} in formulae X and Xa are preferably F, Cl or Br, more preferably Cl or Br and, most preferably, each Cl.

In a preferred embodiment of this invention, T_3 is a hydrogen atom, or T_3 is a hydrocarbon radical defined within the scope of this invention containing 1 to 16, more preferably 1 to 12, carbon atoms.

T_3 defined as alkyl may preferably contain 1 to 8 and, particularly preferably, 1 to 6 carbon atoms. Some examples of alkyl are methyl, ethyl and the isomers of propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl and dodecyl. T_3 is particularly preferably linear C_1-C_4alkyl.

T_3 defined as cycloalkyl may preferably contain 5 to 8 carbon atoms. Cyclopentyl and cyclohexyl are particularly preferred.

T_3 defined as heterocycloalkyl may preferably contain 4 or 5 carbon atoms and is preferably a hetero atom selected from the group consisting of -O-, -S- and -N- . Some examples are tetrahydrofuranyl, pyrrolidinyl, piperazinyl and tetrahydrothiophenyl. Heterocycloalkyl and aryl are preferably linked via a carbon atom of the ring.

T_3 defined as aryl may preferably contain 6 to 10 carbon atoms. Preferred examples are naphthyl and, in particular, phenyl, as well as phenyl which is substituted by C_1-C_4alkyl, C_1-C_4alkoxy or Cl, typically p-methylphenyl, p-ethylphenyl, p-n- or p-i-propylphenyl, p-n-, p-i- or p-t-butylphenyl, p-chlorophenyl and p-methoxyphenyl.

T_3 defined as heteroaryl may preferably contain 4 or 5 carbon atoms and one or two hetero atoms selected from the group consisting of -O-, -S- and -N- . Some examples are furanyl, thiophenyl, pyrrolyl, pyridinyl and pyrimidinyl.

Preferred substituents for T_3 are methyl, ethyl, n- and i-propyl, n-, i- and t-butyl, methoxy, ethoxy, trichloromethyl, trifluoromethyl, phenyl, phenyloxy, F and Cl.

In a preferred embodiment of this invention, T_3 is H, C_1-C_4alkyl, cyclopentyl, cyclohexyl, phenyl or naphthyl, each of which is unsubstituted or substituted by C_1-C_4alkyl, C_1-C_4-alkoxy, C_1-C_4haloalkyl, phenyl, F or Cl.

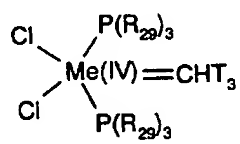
T_4 in formula Xa defined as arene preferably contains 6 to 12 carbon atoms and, defined as heteroarene, preferably 4 to 11 carbon atoms, and preferably contains 1 to 3 hetero atoms selected from the group consisting of O, S and N. Some examples of substituents for T_4 are methyl, ethyl, n- or i-propyl, n-, i- or t-butyl, methoxy, ethoxy, trifluoromethyl, F and Cl. Preferred arenes and heteroarenes are benzene, toluene, xylene, trimethylbenzene, naphthalene, biphenyl, anthracene, acenaphthene, fluorene, phenantrene, pyrene, chrysene, fluoroanthrene, furan, thiophene, pyrrole, pyridine, γ-pyran, γ-thiopyran, pyrimidine, pyrazine, indole, coumarone, thionaphthene, carbazole, dibenzofuran, dibenzothiophene, pyrazole, imidazole, benzimidazole, oxazole, thiazole, isooxazole, isothiazole, quinoline, isoquinoline, acridine, chromene, phenazine, phenoxazine, phenothiazine, triazine, thianthrene, and purine. Particularly preferred arenes and heteroarenes are benzene, naphthalene, cumene, thiophene and benzthiophene. Arene is very particularly preferably benzene

or benzene substituted by C_1-C_4alkyl, such as toluene, xylene, isopropylbenzene, tertiary butylbenzene or cumene; and heteroarene is particularly preferably thiophene.

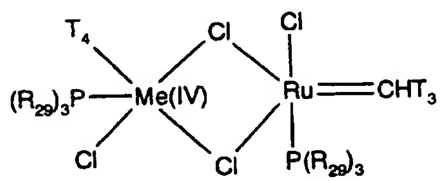
The phosphine group T_1 and T_2 is preferably tertiary phosphines or ditertiary diphosphines containing 3 to 40, more preferably 3 to 30 and, particularly preferably, 3 to 24, carbon atoms.

The tertiary phosphine and ditertiary diphosphine groups have the meanings and preferred meanings stated above for formulae VII and VIIa.

A preferred subgroup of the compounds of formulae X and Xa are those of formulae Xb and Xc



(Xb),



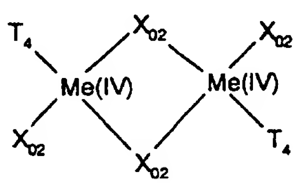
(Xc),

wherein Me is Ru, R_{29} is α-branched C_3-C_8alkyl, C_5-C_8cycloalkyl which is unsubstituted or substituted by C_1-C_4alkyl, C_1-C_4haloalkyl, C_1-C_4alkoxy, halogen or $-NO_2$, or C_6-C_{10}aryl which is unsubstituted or substituted by C_1-C_4alkyl, C_1-C_4haloalkyl, C_1-C_4alkoxy, halogen or $-NO_2$, T_3 is H, C_1-C_8alkyl, C_5-C_8cycloalkyl which is unsubstituted or substituted by C_1-C_4alkyl, C_1-C_4haloalkyl, C_1-C_4alkoxy, halogen or $-NO_2$, or C_6-C_{10}aryl which is unsubstituted or substituted by C_1-C_4alkyl, C_1-C_4haloalkyl, C_1-C_4alkoxy, halogen or $-NO_2$, and T_4 is phenyl or phenyl substituted by 1 to 3 C_1-C_4alkyl.

Some specific and preferred examples are [Me signifies Ru(IV)]:

$Cl_2[P(C_6H_{11})_3]_2Me{=}CH{-}C_6H_5$, $Cl_2[P(C_5H_9)_3]_2Me{=}CH{-}C_6H_5$, $Br_2[P(C_6H_{11})_3]_2Me{=}CH{-}C_6H_5$, $Br_2[P(C_5H_9)_3]_2Me{=}CH{-}C_6H_5$, $F_2[P(C_6H_{11})_3]_2Me{=}CH{-}C_6H_5$, $F_2[P(C_5H_9)_3]_2Me{=}CH{-}C_6H_5$, $Cl_2[P(C_6H_{11})_3]_2Me{=}CH(C_6H_4{-}Cl)$, $Cl_2[P(C_5H_9)_3]_2Me{=}CH(C_6H_4{-}Br)$, $Br_2[P(C_6H_{11})_3]_2Me{=}CH(C_6H_4{-}NO_2)$, $Br_2[P(C_5H_9)_3]_2Me{=}CH(C_6H_4{-}OC_2H_5)_2$, $Cl_2[P(C_6H_{11})_3]_2Me{=}CH(C_6H_4{-}CH_3)$, $F_2[P(C_5H_9)_3]_2Me{=}CH{-}[C_6H_3{-}(CH_3)_2]$, $Cl_2[P(C_6H_{11})_3]_2Me{=}CH{-}C_{10}H_9$, $Cl_2[P(C_5H_9)_3]_2Me{=}CH{-}CH_3$, $Cl_2[P(C_6H_{11})_3]_2Me{=}CHCH_3$, $Br_2[P(C_5H_9)_3]_2Me{=}CH{-}i{-}C_3H_7$, $Cl_2[P(C_6H_{11})_3]_2Me{=}CH{-}t{-}C_4H_9$, $Cl_2[P(C_5H_9)_3]_2Me{=}CH{-}n{-}C_4H_9$, $Cl_2[P(C_6H_{11})_3]_2Me{=}CH{-}C_6H_4{-}OCH_3$, $Cl_2[P(C_5H_9)_3]_2Me{=}CH{-}C_6H_3{-}(CH_3)_2$, $Br_2[P(C_6H_{11})_3]_2Me{=}CH{-}C_6H_2{-}(CH_3)_3$, $Br_2[P(C_5H_9)_3]_2Me{=}CH{-}CH_2C_6H_5$, $Cl_2[P(t{-}C_4H_9)_3]_2Me{=}CH{-}C_6H_5$, $Cl_2[P(i{-}C_3H_7)_3]_2Me{=}CH{-}C_6H_5$, $Cl_2[P(C_6H_5)_3]_2Me{=}CH{-}C_6H_5$, $Cl_2[P(C_6H_3{-}CH_3)_3]_2Me{=}CH{-}C_6H_5$, $Br_2[P(C_5H_4{-}(CH_3)_2)_3]_2Me{=}CH{-}C_6H_5$, $Cl_2[P(C_6H_3{-}(CH_3)_3]_2Me{=}CH{-}C_6H_5$, $Cl_2[P(C_6H_{11})_3{-}CH_2CH_2{-}P(C_6H_{11})_3]Me{=}CH{-}C_6H_5$, $Cl_2[P(C_5H_9)_3]_2Me{=}CH{-}C_6H_{11}$, $Cl_2[P(C_5H_9)_3]_2Me{=}CH{-}C_5H_9$, $Cl_2[P(C_5H_9)_3]_2Me{=}C(C_6H_{11})_2$, $Cl_2[P(C_6H_{11})_3]_2Me{=}CH_2$, $Cl_2[P(C_5H_9)_3]_2Me{=}CH_2$, $Cl_2[P(C_6H_{11})_3]_2Me{=}CH$-n-butyl, $Cl_2[P(i{-}C_3H_7)_3]_2Me{=}CH{-}C_6H_5$, $Cl_2[P(i{-}C_3H_7)_3]_2Me{=}CH{-}C_5H_{11}$.

The compounds of formula X are known and their preparation is described by P. Schwab et al. in Angew. Chem. (1995), 107, No. 18, pages 2179 to 2181. The binuclear compounds of formula Xa can be prepared, for example, by reacting 2 equivalents of a compound of formula X with one equivalent of a per se known compound of formula



wherein X_{02}, Me and T_4 have the meanings stated for formula Xa, in the presence of an inert solvent.

Particularly preferred novel mixtures are those, wherein the ruthenium catalyst A conforms to formula IXe,

$$(R_{26}R_{27}R_{28}P)L_1Ru^{2+}(Z_1^{1-})_2 \qquad \text{(IXe)},$$

wherein R_{26}, R_{27} and R_{28} have the meanings stated above, including the preferred meanings, L_1 is an arene or heteroarene, including the preferred meanings stated above, and Z_1^{1-} is Cl^-, Br^-, BF_4^-, PF_6^-, SbF_6^-, AsF_6^-, $CF_3SO_3^-$, C_6H_5-SO_3^-, 4-methyl-C_6H_5-SO_3^-, 3,5-dimethyl-C_6H_5-SO_3^-, 2,4,6-trimethyl-C_6H_5-SO_3^- or 4-CF_3-C_6H_5-SO_3^- ;
and the ruthenium carbene catalyst B conforms to formula X and, particularly preferably, to formula Xb.

The novel mixtures are excellently suitable as catalysts for the ring-opening metathesis polymerisation of strained cycloolefins.

In another of its aspects, the invention relates to a composition consisting of (a) at least one strained cycloolefin and (b) a catalytically effective amount of a mixture of at least one thermal carbene-free ruthenium catalyst A and at least one thermal ruthenium carbene catalyst B, both of which initiate the ring-opening metathesis polymerisation on their own, said catalysts being present in a weight ratio of A to B from 10:1 to 1:10. The catalysts in the novel compositions have the same preferred meanings as described above.

Catalytically effective signifies that the mixture is used in amounts which give, at a defined polymerisation cycle for a specific cycloolefin (see Examples), shaped articles having better physical and mechanical properties than when half the amount is used as individual components.

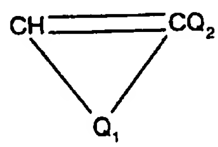
In a preferred embodiment of this invention, the amount of the novel mixture in the composition is from 0.05 to 0.3 % by weight, preferably from 0.05 to 0.25 % by weight and, most preferably, from 0.1 to 0.2 % by weight, based on the amount of the cycloolefins present.

The cyclic olefins may be monocyclic or polycyclic condensed and/or bridged and/or linked ring systems, for example having from two to four rings, which are unsubstituted or substituted and may contain hetero atoms, for example an O, S, N or Si atom, in one or more than one ring and/or may contain condensed aromatic or heteroaromatic rings, for example o-phenylene, o-naphthylene, o-pyridinylene or o-pyrimidinylene. The individual cyclic rings may contain from 3 to 16, preferably from 3 to 12 and, particularly preferably, from 3 to 8, ring members. The cyclic olefins may contain further non-aromatic double bonds, preferably, depending on the ring size, from 2 to 4 such additional double bonds. The ring sub-

stituents are inert, that is to say they do not adversely affect the chemical stability and the thermal stability of the ruthenium and osmium catalysts. The cycloolefins are strained rings or ring systems. Individual rings and ring systems having from 5 to 8 carbon atoms in the ring are particularly preferred.

When the cyclic olefins contain more than one double bond, for example from 2 to 4 double bonds, or when mixtures of strained cycloolefins having one double bond and strained cycloolefins having at least two double bonds; for example from 2 to 4 double bonds, are used, then, depending on the reaction conditions, the monomer chosen and the amount of catalyst, it is also possible for crosslinked polymers to be formed.

In a preferred embodiment of the composition according to the invention, the cycloolefins conform to formula II



(II),

wherein

Q_1 is a radical having at least one carbon atom which, together with the $-CH=CQ_2-$ group, forms an at least 3-membered alicyclic ring which may contain one or more than one hetero atom selected from the group consisting of Si, P, O, N and S; and which is unsubstituted or substituted by halogen, =O, -CN, $-NO_2$, $R_1R_2R_3Si-(O)_u-$, -COOM, $-SO_3M$, $-PO_3M$, $-COO(M_1)_{1/2}$, $-SO_3(M_1)_{1/2}$, $-PO_3(M_1)_{1/2}$, C_1-C_{20}alkyl, C_1-C_{20}hydroxyalkyl, C_1-C_{20}haloalkyl, C_1-C_6cyanoalkyl, C_3-C_8cycloalkyl, C_6-C_{16}aryl, C_7-C_{16}aralkyl, C_3-C_6-heterocycloalkyl, C_3-C_{16}heteroaryl, C_4-C_{16}heteroaralkyl or by R_4-X-; or wherein two adjacent carbon atoms, when present, are substituted by -CO-O-CO- or by $-CO-NR_5-CO-$; or wherein an alicyclic, aromatic or heteroaromatic ring has been fused to adjacent carbon atoms of the alicyclic ring, the former ring being unsubstituted or substituted by halogen, -CN, $-NO_2$, $R_6R_7R_8Si-(O)_u-$, -COOM, $-SO_3M$, $-PO_3M$, $-COO(M_1)_{1/2}$, $-SO_3(M_1)_{1/2}$, $-PO_3(M_1)_{1/2}$, C_1-C_{20}alkyl, C_1-C_{20}haloalkyl, C_1-C_{20}hydroxyalkyl, C_1-C_6cyanoalkyl, C_3-C_8cycloalkyl, C_6-C_{16}aryl, C_7-C_{16}aralkyl, C_3-C_6heterocycloalkyl, C_3-C_{16}heteroaryl, C_4-C_{16}heteroaralkyl or by R_{13}-X_1-; X and X_1 are each independently of

the other -O-, -S-, -CO-, -SO-, $-SO_2-$, -O-C(O)-, -C(O)-O-, $-C(O)-NR_5-$, $-NR_{10}-C(O)-$, $-SO_2-O-$ or $-O-SO_2-$; R_1, R_2 and R_3 are each independently of one another C_1-C_{12}alkyl, C_1-C_{12}perfluoroalkyl, phenyl or benzyl; R_4 and R_{13} are each independently of the other C_1-C_{20}alkyl, C_1-C_{20}haloalkyl, C_1-C_{20}hydroxyalkyl, C_3-C_8cycloalkyl, C_6-C_{16}aryl or C_7-C_{16}-aralkyl; R_5 and R_{10} are each independently of the other hydrogen, C_1-C_{12}alkyl, phenyl or benzyl, the alkyl groups in turn being unsubstituted or substituted by C_1-C_{12}alkoxy or by C_3-C_8cycloalkyl; R_6, R_7 and R_8 are each independently of one another C_1-C_{12}alkyl, C_1-C_{12}perfluoroalkyl, phenyl or benzyl; M is an alkali metal and M_1 is an alkaline earth metal; and u is 0 or 1; it being possible for the alicyclic ring formed with Q_1 to contain further non-aromatic double bonds;

Q_2 is hydrogen, C_1-C_{20}alkyl, C_1-C_{20}haloalkyl, C_1-C_{12}alkoxy, halogen, -CN or R_{11}-X_2- , wherein R_{11} is C_1-C_{20}alkyl, C_1-C_{20}haloalkyl, C_1-C_{20}hydroxyalkyl, C_3-C_8cycloalkyl, C_6-C_{16}aryl or C_7-C_{16}aralkyl, and X_2 is -C(O)-O- or $-C(O)-NR_{12}-$, wherein R_{12} is hydrogen, C_1-C_{12}alkyl, phenyl or benzyl;

the above-mentioned cycloalkyl, heterocycloalkyl, aryl, heteroaryl, aralkyl and heteroaralkyl groups being unsubstituted or substituted by C_1-C_{12}alkyl, C_1-C_{12}alkoxy, $-NO_2$, -CN or by halogen, and the hetero atoms of the above-mentioned heterocycloalkyl, heteroaryl and heteroaralkyl groups being selected from the group consisting of -O-, -S-, $-NR_9-$ and -N=; and R_9 is hydrogen, C_1-C_{12}alkyl, phenyl or benzyl.

Fused alicyclic rings contain preferably from 3 to 8, more preferably from 5 to 8 and, most preferably, 5 or 6, ring carbon atoms.

When an asymmetric centre is present in the compounds of formula I, the compounds may occur in optically isomeric forms. Some compounds of formula I may occur in tautomeric forms (for example keto-enol tautomerism). When an aliphatic C=C double bond is present, geometric isomerism (E-form or Z-form) may also occur. Exo-endo configurations are also possible. Formula I therefore includes all possible stereoisomers present in the form of enantiomers, tautomers, diastereoisomers, E/Z-isomers or mixtures thereof.

In the definitions of the substituents, the alkyl, alkenyl and alkynyl groups may be straight-chain or branched. The same applies also to the (or each) alkyl moiety of alkoxy, alkylthio and alkoxycarbonyl and other alkyl-containing groups. These alkyl groups contain preferably from 1 to 12, more preferably from 1 to 8 and, most preferably, from 1 to 4, carbon

atoms. These alkenyl and alkynyl groups contain preferably from 2 to 12, more preferably from 2 to 8 and, most preferably, from 2 to 4, carbon atoms.

Alkyl includes, for example, methyl, ethyl, isopropyl, n-propyl, n-butyl, isobutyl, tert-butyl and the various isomeric pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, nonadecyl and eicosyl radicals.

Hydroxyalkyl includes, for example, hydroxymethyl, hydroxyethyl, 1-hydroxyisopropyl, 1-hydroxy-n-propyl, 2-hydroxy-n-butyl, 1-hydroxyisobutyl, 1-hydroxy-sec-butyl, 1-hydroxy-tert-butyl and the various isomeric pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, nonadecyl and eicosyl radicals.

Haloalkyl includes, for example, fluoromethyl, difluoromethyl, trifluoromethyl, chloromethyl, dichloromethyl, trichloromethyl, 2,2,2-trifluoroethyl, 2-fluoroethyl, 2-chloroethyl, 2,2,2-trichloroethyl and also halogenated, preferably fluorinated or chlorinated, alkanes, for example isopropyl, n-propyl, n-butyl, isobutyl, sec-butyl, tert-butyl and the various isomeric pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, nonadecyl and eicosyl radicals.

Alkenyl includes, for example, propenyl, isopropenyl, 2-butenyl, 3-butenyl, isobutenyl, n-penta-2,4-dienyl, 3-methyl-but-2-enyl, n-oct-2-enyl, n-dodec-2-enyl, isododecenyl, n-octadec-2-enyl and n-octadec-4-enyl.

Cycloalkyl is preferably C_5-C_8cycloalkyl, in particular C_5- or C_6cycloalkyl. Some examples are cyclopropyl, dimethylcyclopropyl, cyclobutyl, cyclopentyl, methylcyclopentyl, cyclohexyl, cycloheptyl and cyclooctyl.

Cyanoalkyl includes, for example, cyanomethyl (methylnitrile), cyanoethyl (ethylnitrile), 1-cyanoisopropyl, 1-cyano-n-propyl, 2-cyano-n-butyl, 1-cyano-isobutyl, 1-cyano-sec-butyl, 1-cyano-tert-butyl and the various isomeric cyanopentyl and cyanohexyl radicals.

Aralkyl contains preferably from 7 to 12 carbon atoms and, more preferably, from 7 to 10 carbon atoms. It may be, for example, benzyl, phenethyl, 3-phenylpropyl, α-methylbenzyl, phenbutyl or α,α-dimethylbenzyl.

Aryl preferably contains from 6 to 10 carbon atoms. It may be, for example, phenyl, pentaline, indene, naphthalene, azulene or anthracene.

Heteroaryl preferably contains 4 or 5 carbon atoms and one or two hetero atoms from the group O, S and N. It may be, for example, pyrrole, furan, thiophene, oxazole, thiazole, pyridine, pyrazine, pyrimidine, pyridazine, indole, purine or quinoline.

Heterocycloalkyl preferably contains 4 or 5 carbon atoms and one or two hetero atoms from the group O, S and N. It may be, for example, oxirane, azirine, 1,2-oxathiolane, pyrazoline, pyrrolidine, piperidine, piperazine, morpholine, tetrahydrofuran or tetrahydrothiophene.

Alkoxy is, for example, methoxy, ethoxy, propyloxy, isopropyloxy, n-butyloxy, isobutyloxy and tert-butyloxy.

Within the scope of this invention, an alkali metal is to be understood as being lithium, sodium, potassium, rubidium or caesium, preferably lithium, sodium or potassium.

Within the scope of this invention, an alkaline earth metal will be understood as being beryllium, magnesium, calcium, strontium or barium, preferably magnesium or calcium.

In the above definitions, halogen will be understood as being fluoro, chloro, bromo or iodo, preferably fluoro, chloro or bromo.

Compounds of formula II that are particularly suitable for the composition according to the invention are those wherein Q_2 is hydrogen.

Also preferred for the composition are compounds of formula II in which the alicyclic ring formed by Q_1 together with the $-CH=CQ_2-$ group has from 3 to 16, preferably from 3 to 12,

more preferably from 3 to 8, and, most preferably, from 5 to 8, ring atoms, and which may be monocyclic, bicyclic, tricyclic or tetracyclic ring systems.

It is especially advantageous when the composition according to the invention comprises compounds of formula II, wherein

Q_1 is a radical having at least one carbon atom which, together with the -CH=CQ_2- group, forms a 3- to 20-membered alicyclic ring which may contain one or more than one hetero atom selected from the group Si, O, N and S; and which is unsubstituted or substituted by halogen, =O, -CN, -NO_2, $R_1R_2R_3Si$-$(O)_u$-, -COOM, -SO_3M, -PO_3M, -$COO(M_1)_{1/2}$, -$SO_3(M_1)_{1/2}$, -$PO_3(M_1)_{1/2}$, C_1-C_{12}alkyl, C_1-C_{12}haloalkyl, C_1-C_{12}hydroxyalkyl, C_1-C_4cyanoalkyl, C_3-C_6cycloalkyl, C_6-C_{12}aryl, C_7-C_{12}aralkyl, C_3-C_6heterocycloalkyl, C_3-C_{12}heteroaryl, C_4-C_{12}heteroaralkyl or by R_4-X-; or wherein two adjacent carbon atoms in that radical Q_1 are substituted by -CO-O-CO- or by -CO-NR_5-CO-; or wherein an alicyclic, aromatic or heteroaromatic ring may have been fused to adjacent carbon atoms, which ring is unsubstituted or substituted by halogen, -CN, -NO_2, $R_6R_7R_8Si$-, -COOM, -SO_3M, -PO_3M, -$COO(M_1)_{1/2}$, -$SO_3(M_1)_{1/2}$, -$PO_3(M_1)_{1/2}$, C_1-C_{12}alkyl, C_1-C_{12}-haloalkyl, C_1-C_{12}hydroxyalkyl, C_1-C_4cyanoalkyl, C_3-C_6cycloalkyl, C_6-C_{12}aryl, C_7-C_{12}-aralkyl, C_3-C_6heterocycloalkyl, C_3-C_{12}heteroaryl, C_4-C_{12}heteroaralkyl or by R_{13}-X_1-; X and X_1 are each independently of the other -O-, -S-, -CO-, -SO-, -SO_2-, -O-C(O)-, -C(O)-O-, -C(O)-NR_5-, -NR_{10}-C(O)-, -SO_2-O- or -O-SO_2-; and R_1, R_2 and R_3 are each independently of one another C_1-C_6alkyl, C_1-C_6perfluoroalkyl, phenyl or benzyl; M is an alkali metal and M_1 is an alkaline earth metal; R_4 and R_{13} are each independently of the other C_1-C_{12}alkyl, C_1-C_{12}haloalkyl, C_1-C_{12}hydroxyalkyl, C_3-C_8cycloalkyl, C_6-C_{12}aryl or C_7-C_{12}aralkyl; R_5 and R_{10} are each independently of the other hydrogen, C_1-C_6alkyl, phenyl or benzyl, the alkyl groups in turn being unsubstituted or substituted by C_1-C_6-alkoxy or by C_3-C_6cycloalkyl; R_6, R_7 and R_8 are each independently of the other C_1-C_6alkyl, C_1-C_6perfluoroalkyl, phenyl or benzyl; u is 0 or 1; it being possible for the alicyclic ring formed with Q_1 to contain further non-aromatic double bonds;

Q_2 is hydrogen, C_1-C_{12}alkyl, C_1-C_{12}haloalkyl, C_1-C_6alkoxy, halogen, -CN or R_{11}-X_2- , wherein R_{11} is C_1-C_{12}alkyl, C_1-C_{12}haloalkyl, C_1-C_{12}hydroxyalkyl, C_3-C_6cycloalkyl, C_6-C_{12}aryl or C_7-C_{12}aralkyl, and X_2 is -C(O)-O- or -C(O)-NR_{12}- , wherein R_{12} is hydrogen, C_1-C_6alkyl, phenyl or benzyl;

and the cycloalkyl, heterocycloalkyl, aryl, heteroaryl, aralkyl and heteroaralkyl groups being unsubstituted or substituted by C_1-C_6alkyl, C_1-C_6alkoxy, -NO_2, -CN or by halogen, and the

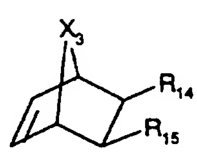
hetero atoms of the heterocycloalkyl, heteroaryl and heteroaralkyl groups being selected from the group consisting of -O-, -S-, $-NR_9-$ and -N=; and R_9 is hydrogen, C_1-C_6alkyl, phenyl or benzyl.

From that group preference is given to those compounds of formula II, wherein

Q_1 is a radical having at least one carbon atom which, together with the $-CH=CQ_2-$ group, forms a 3- to 10-membered alicyclic ring which may contain a hetero atom selected from the group Si, O, N and S, and which is unsubstituted or substituted by halogen, -CN, $-NO_2$, $R_1R_2R_3Si-$, -COOM, $-SO_3M$, $-PO_3M$, $-COO(M_1)_{1/2}$, $-SO_3(M_1)_{1/2}$, $-PO_3(M_1)_{1/2}$, C_1-C_6alkyl, C_1-C_6haloalkyl, C_1-C_6hydroxyalkyl, C_1-C_4cyanoalkyl, C_3-C_6cycloalkyl, phenyl, benzyl or by R_4-X-; or wherein an alicyclic, aromatic or heteroaromatic ring may have been fused to adjacent carbon atoms, which ring is unsubstituted or substituted by halogen, -CN, $-NO_2$, $R_6R_7R_8Si-$, -COOM, $-SO_3M$, $-PO_3M$, $-COO(M_1)_{1/2}$, $-SO_3(M_1)_{1/2}$, $-PO_3(M_1)_{1/2}$, C_1-C_6alkyl, C_1-C_6haloalkyl, C_1-C_6hydroxyalkyl, C_1-C_4cyanoalkyl, C_3-C_6cycloalkyl, phenyl, benzyl or by R_{13}-X_1-; R_1, R_2 and R_3 are each independently of one another C_1-C_4alkyl, C_1-C_4perfluoroalkyl, phenyl or benzyl; M is an alkali metal and M_1 is an alkaline earth metal; R_4 and R_{13} are each independently of the other C_1-C_6alkyl, C_1-C_6haloalkyl, C_1-C_6hydroxyalkyl or C_3-C_6cycloalkyl; X and X_1 are each independently of the other -O-, -S-, -CO-, -SO- or $-SO_2-$; R_6, R_7 and R_8 are each independently of one another C_1-C_4alkyl, C_1-C_4perfluoroalkyl, phenyl or benzyl; and

Q_2 is hydrogen.

The composition according to the invention preferably comprises norbornene and norbornene derivatives, norbornadiene, cyclopentene, cycloheptene, cyclooctene, cyclooctadiene or cyclododecene. Of the norbornene derivatives, special preference is given to those corresponding to formula III



(III),

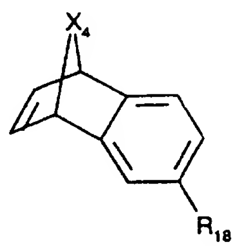
wherein

X_3 is $-CHR_{16}-$, oxygen or sulfur;

R_{14} and R_{15} are each independently of the other hydrogen, -CN, trifluoromethyl, $(CH_3)_3Si-O-$, $(CH_3)_3Si-$ or $-COOR_{17}$; and

R_{16} and R_{17} are each independently of the other hydrogen, C_1-C_{12}alkyl, phenyl or benzyl;

or to formula IV



(IV),

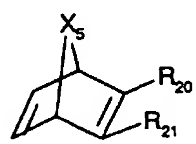
wherein

X_4 is -CHR_{19}-, oxygen or sulfur;

R_{18} is hydrogen, C_1-C_6alkyl or halogen; and

R_{19} is hydrogen, C_1-C_{12}alkyl, phenyl or benzyl;

or to formula V



(V),

wherein

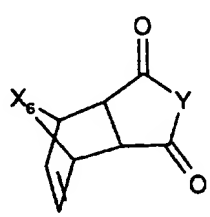
X_5 is -CHR_{22}-, oxygen or sulfur;

R_{20} and R_{21} are each independently of the other hydrogen, CN, trifluoromethyl, $(CH_3)_3Si$-O-, $(CH_3)_3Si$- or -$COOR_{23}$; and

R_{22} is hydrogen, C_1-C_{12}alkyl, phenyl or benzyl;

R_{23} is hydrogen, C_1-C_{12}alkyl, phenyl or benzyl;

or to formula VI,



(VI),

wherein

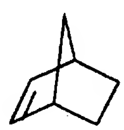
X_6 is -CHR_{24}-, oxygen or sulfur;

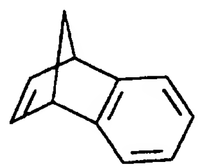
Y is oxygen or $>N-R_{25}$,

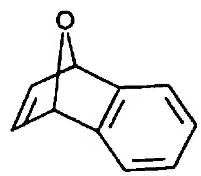
R_{24} is hydrogen, C_1-C_{12}alkyl, phenyl or benzyl; and
R_{25} is hydrogen, methyl, ethyl or phenyl.

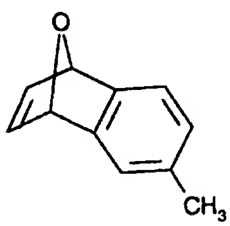
Another preferred subgroup of monomers is formed by those composed only of carbon and hydrogen.

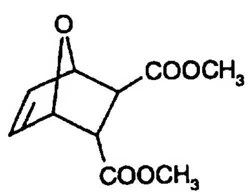
The following compounds of formula I which may be preparable by Diels-Alder reactions are some specific examples, it being possible for the oxanorbornene derivatives also to be norbornene derivatives and vice versa:

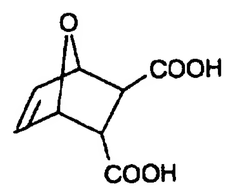


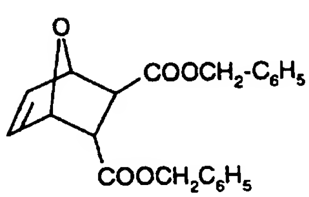


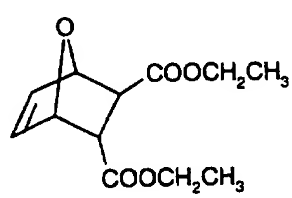


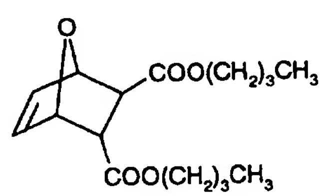


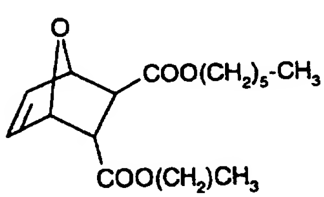


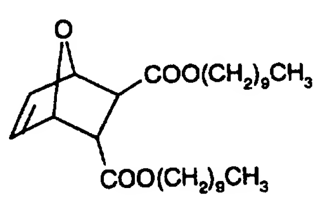


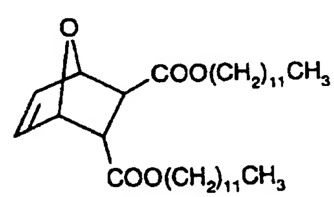


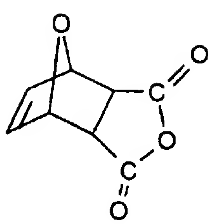
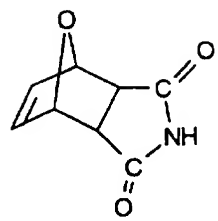
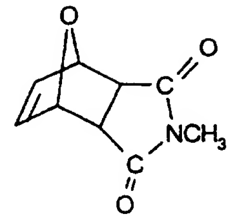
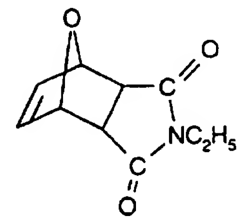


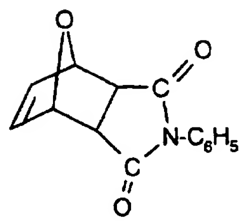
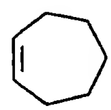
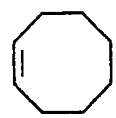
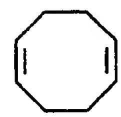
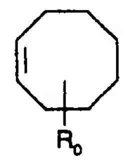


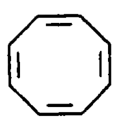
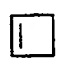


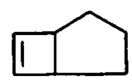
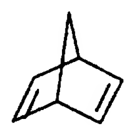


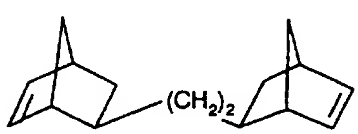
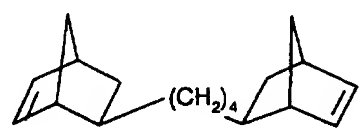


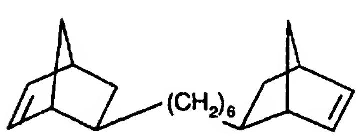
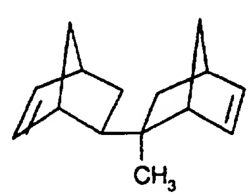
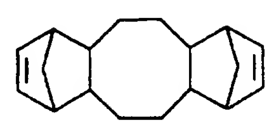





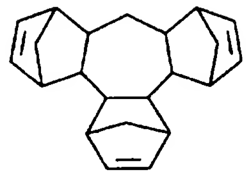






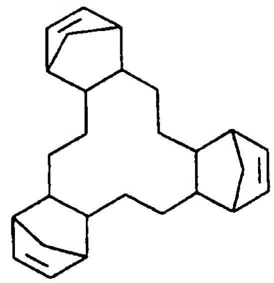



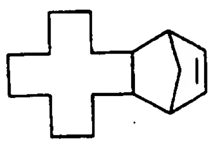



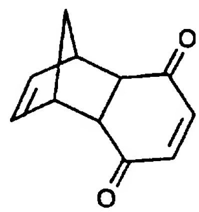







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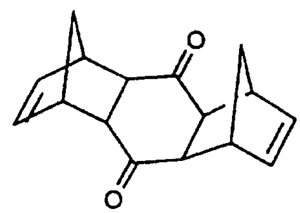
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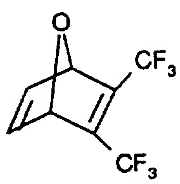
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CF3
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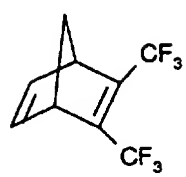
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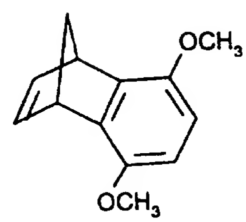
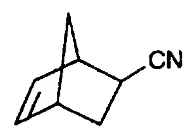
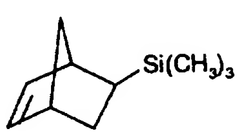
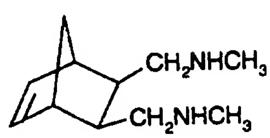
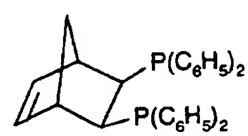
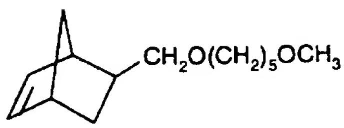

OCH3
OCH3

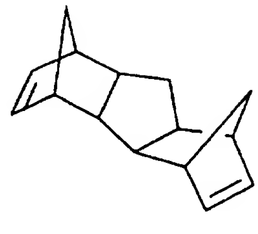

CN

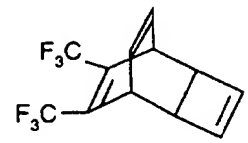

Si(CH3)3

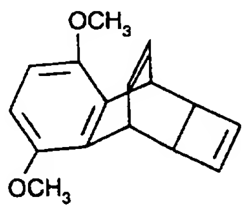

CH2NHCH3
CH2NHCH3


P(C6H5)2
P(C6H5)2





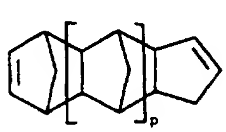




R_0 can, for example, be an epoxy, acrylate or methacrylate group which is covalently bonded to the cyclooctene directly or via a bridge group.

Condensed and/or bridged and/or linked olefinically unsaturated ring systems are generally prepared by means of Diels-Alder reactions. They should be fusable without decomposition which, within the scope of the invention, means that strained cycloolefins can be fused and the catalyst can be dissolved. In the case of thermally labile strained cycloolefins it may therefore be necessary to dissolve the catalyst under pressure. Where the reaction temperature is higher than the decomposition temperature of the strained cycloolefin, it is advisable to carry out the procedures under pressure in order to avoid decomposition of the monomers prior to polymerisation.

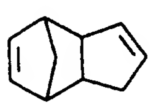
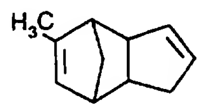
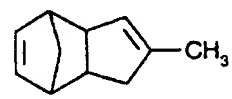
A preferred subgroup are the Diels-Alder adducts of cyclopentadienes, many of which are known and are commercially available (they are obtained, for example, in petroleum distillation), or which can be prepared in known manner by a Diels-Alder reaction of cyclopentadienes with cyclopentadienes, or with Diels-Alder adducts of cyclopentadienes (oligocyclopentadienes). These Diels-Alder adducts can conform to formula I

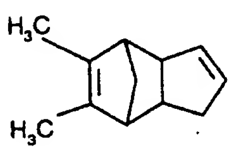
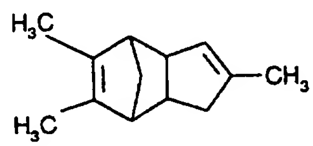
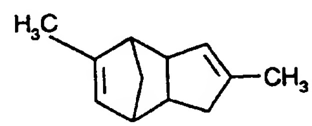


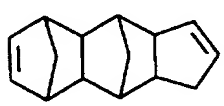
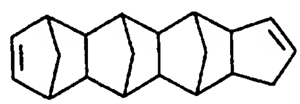
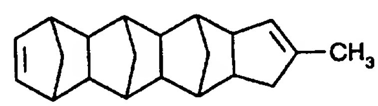
(I),

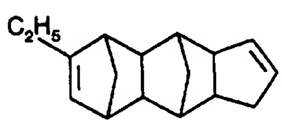
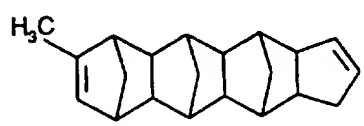
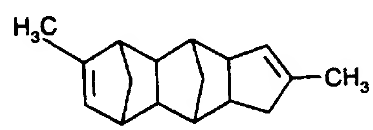
wherein p is 0 or a number from 1 to 100, preferably from 1 to 50, particularly preferably from 1 to 20 and, most preferably, from 1 to 10, and wherein the adduct may be substituted as stated above for the Diels-Alder adducts, preferably by C_1-C_6alkyl groups.

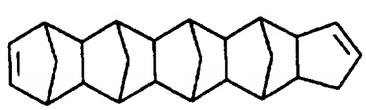
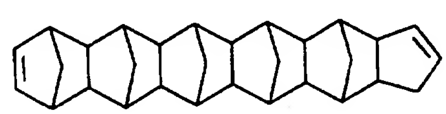
Illustrative examples of compounds of formula I are

 ,  ,  ,

 ,  ,  ,

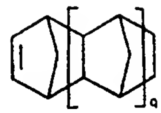
 ,  ,  ,

 ,  ,  ,

 ,  ,

as well as tricyclopentadiene.

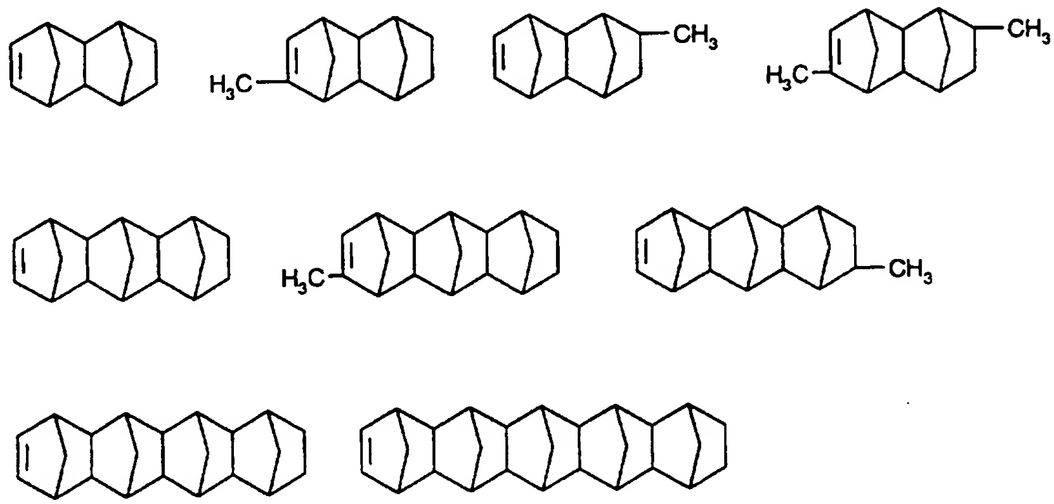
Another preferred subgroup of Diels-Alder adducts are those of unsubstituted or substituted norbornenes or norbornadienes with unsubstituted or substituted 1,3-cyclopentadienes. Particularly preferred Diels-Alder adducts are those of formula Ia



(Ia),

wherein q is preferably a number from 1 to 20, more preferably from 1 to 10 and, particularly preferably, from 1 to 5, the Diels-Alder adducts being unsubstituted or substituted by, preferably, C_1-C_6alkyl.

Illustrative examples of compounds of formula Ia are



The composition according to the invention may additionally contain further open-chain comonomers that form copolymers with the strained cycloolefins. When dienes are additionally used, for example, crosslinked polymers may be formed. Some examples of such comonomers are olefinically mono- or di-unsaturated compounds, such as olefins and dienes from the group ethene, propene, butene, pentene, hexene, heptene, octene, decene, dodecylene, cyclohexene (which, as is known, does not form metathesis polymers on its own), acrylic and methacrylic acid and the esters and amides thereof, vinyl ethers, vinyl esters, vinyl chloride, vinylidene chloride, styrene, butadiene, isoprene and chlorobutadiene. When volatile comonomers are additionally used, it is often necessary to carry out the procedures

under pressure. The additional use of non-volatile comonomers can therefore be of advantage to the method.

The further open-chain olefins suitable for copolymerisation are present in the novel composition in an amount of typically up to 80 % by weight, preferably from 0.1 to 80 % by weight, more preferably from 0.5 to 60 % by weight and, most preferably, from 5 to 40 % by weight, based on the total amount of compounds of di- and oligocyclopentadienes and further olefins capable of copolymerisation.

The composition according to the invention may contain formulation auxiliaries. Known auxiliaries are antistatics, antioxidants, light stabilisers, plasticisers, dyes, pigments, fillers, reinforcing fillers, lubricants, adhesion promoters, viscosity-increasing agents and demoulding auxiliaries. The fillers may be present in surprisingly high proportions without having an adverse effect on the polymerisation, for example in amounts of up to 80 % by weight, preferably from 1 to 70 % by weight, more preferably from 5 to 70 % by weight, particularly preferably from 5 to 60 % by weight and, most preferably, from 10 to 60 % by weight, based on the composition. A great variety of fillers and reinforcing fillers for improving the optical, physical, mechanical and electrical properties is known. Some examples are glass and quartz in the form of powders, beads and fibres, metal and semi-metal oxides, carbonates such as $MgCO_3$, $CaCO_3$, dolomite, metal sulfates such as gypsum and barite, natural and synthetic silicates such as talc, zeolites, wollastonite, feldspars, argillaceous earths, such as China clay, crushed stone, whiskers, carbon fibres, plastics fibres or powders, and carbon black. Viscosity-increasing agents are in particular metathesis polymers that have olefinically unsaturated groups and can be incorporated into the polymer during polymerisation. Such metathesis polymers are known and are commercially available, for example, under the trade name Vestenamere®. For the same purpose it is also possible to use, for example, poly-1,3-dienes such as polybutadiene, polyisoprene, polychlorobutadiene or copolymers with the basic dienes and one or more olefins. Such polymers are also commercially available, for example Buna® and Kraton®. The amount of viscosity-increasing polymers can be, for example, from 0.1 to 50 % by weight, preferably from 1 to 30 % by weight and, preferably, from 1 to 20 % by weight, based on all the monomers present in the composition. The viscosity-increasing agents serve simultaneously to improve the viscous properties

of the polymers. The viscosity of the composition can be adjusted to the desired applications within a wide scope.

The compositions according to the invention are excellently suitable for the direct preparation of shaped articles. Although the catalyst activity is in some cases high, the individual components can be mixed and brought into the desired form because the catalysts dissolve in non-polar and polar monomers even at room temperature or with slight heating. Solubilisers (solvents such as methylene chloride, tetrahydrofuran) can be additionally used and are conveniently removed again before polymerisation. Besides direct preparation of shaped articles, it is also possible to carry out polymerisations in solution or emulsions, the polymers only then being further processed to shaped articles.

In another of its aspects, this invention relates to a process for the preparation of polymers by metathesis polymerisation, which comprises heating a novel composition.

The preferred meanings of the novel process are the same as those of the novel compositions.

The compositions according to the invention are relatively storage-stable, but monomers and catalyst are expediently mixed together only just before processing. The process according to the invention is advantageously carried out in such a manner that shaping, for example to give a coating or a moulding, is combined with the mixing and takes place prior to the polymerisation. In principle, all known shaping procedures, for example extrusion, injection moulding and compression procedures, can be used. The compositions according to the invention are suitable especially as casting resins where appropriate with the application of pressure, for example as in RIM processes (Reaction Injection Moulding).

"Heating" may represent a temperature from 30 to 300°C, preferably from 40 to 300°C, more preferably from 50 to 250°C, particularly preferably from 60 to 250°C and, most preferably, from 60 to 200°C. The polymerisation times depend essentially on the catalyst activity and the times can vary from seconds to minutes up to several hours. The polymerisation can also be carried out stepwise with increasing temperatures.

Using the process according to the invention it is possible to produce materials (semi-finished articles) for the preparation of mouldings by means of machining techniques or to prepare directly all kinds of mouldings, films, foils and coatings. The invention relates also to the use of the novel composition for the preparation of semi-finished articles, mouldings and foils. The invention relates also to mouldings made from the compositions according to the invention.

Depending on the monomer used, the polymers according to the invention may have very different properties. Some are distinguished by a very high degree of oxygen permeability, low dielectric constants, good thermal stability and low water absorption. Others have excellent optical properties, for example high transparency and low refractive indices. Special mention should also be made of the low degree of shrinkage. They can therefore be used in a very wide variety of technical fields. The avoidance of solvents ensures the production of bubble-free mouldings and coatings even at relatively high polymerisation temperatures.

When used as coatings on the surfaces of support materials, in particular non-polar support materials, the novel compositions are distinguished by high adhesive strength. A physical treatment (for example plasma treatment) or chemical treatment (application of adhesion promoters) can further improve the adhesive strength. The coated materials are also distinguished by a very high degree of surface smoothness and gloss. Among their good mechanical properties, special mention should be made of the low degree of shrinkage and the high impact strength, and also the thermal stability. In addition, they can be readily demoulded when processed in moulds and have a high resistance to solvents. The properties desired in final use can be adjusted selectively by way of the monomers chosen. In addition to rigid and resilient thermoplastic mouldings it is also possible to obtain cross-linked thermosetting or elastomeric polymers.

These polymers are suitable for the production of medical apparatus, implants or contact lenses; for the production of electronic components; as binders for surface-coatings; as photocurable compositions for model-making or as adhesives for bonding substrates having low surface energies (for example Teflon, polyethylene and polypropylene).

The compositions according to the invention are particularly suitable for the preparation of protective coatings on substrates or support materials. The invention relates also to a variant of the process according to the invention for the preparation of coatings on support materials in which a composition according to the invention is applied as a coating to a support, for example by means of immersion, spreading, pouring, rolling, knife-application or centrifugal moulding procedures, and the coating is heated for the purpose of polymerisation. This may be followed by heat treatment. Surfaces of substrates can be modified or protected using that method.

This invention relates also to a composition consisting of (a) a support material and (b) a coating of a composition according to the invention which is applied to at least one surface.

This invention relates likewise to a composition consisting of (a) a support material and (b) a polymeric coating of a composition according to the invention which is applied to at least one surface.

Suitable substrates (support materials) are, for example, glass, minerals, ceramics, plastics, wood, semi-metals, metals, metal oxides and metal nitrides. The coating thicknesses depend essentially on the desired use and may be, for example, from 0.1 to 1000 μm, preferably from 0.5 to 500 μm, more preferably from 1 to 100 μm. The coated materials are distinguished by high adhesive strength and good thermal and mechanical properties.

The preparation of the coated materials according to the invention can be carried out in accordance with known methods, for example spreading, knife-application or pouring processes, such as curtain coating or centrifugal moulding.

The compositions according to the invention are suitable also for the preparation of rubber-like or thermoplastic polymers which can be further crosslinked. For that purpose the strained cycloolefins may contain reactive groups, for example (meth)acrylate or epoxy groups, which are covalently bonded to the cycloolefin directly or via a bridge group.

The compositions according to the invention can also be used as thermally curable adhesives for firm bonding to a very wide range of materials, it being possible to achieve excellent peel resistance.

In addition to having high adhesive strengths, excellent processability, good surface properties (smoothness, gloss), high crosslinking density and resistance to solvents and other liquids, the polymers according to the invention are also distinguished in particular by very good physico-mechanical properties, for example high thermal stability, breaking and flexural strength and impact strength, and excellent electrical properties, for example low conductivities, dielectric constants and (ε)- and (tan δ)-loss factors. In addition, mention should be made of the high oxygen permeability and low water absorption. Polymers composed only of carbon and hydrogen are particularly valuable from the ecological standpoint because they can, for example, be completely recycled by pyrolysis or harmlessly burned.

The following Examples illustrate the invention in more detail.

USE EXAMPLES

The following catalysts are used:

[1-methyl-4-isopropylbenzene][$P(C_6H_{11})_3$]Ru(II)Cl_2 (catalyst A).

$Cl_2[P(C_6H_{11})_3]_2$Ru(IV)=CH-C_6H_5 (catalyst B).

[1-methyl-4-isopropylbenzene] [P(n-butyl)$_3$] Ru(II)Cl_2 (catalyst C).

[(1-methyl-4-isopropylbenzene)RuCl_2]$_2$ (catalyst D).

Cl_2[P(iso-C_3H_7)$_3$]$_2$Ru(IV)=CH-C_6H_5 (catalyst E).

Cl_2[P(cyclohexyl)$_3$]$_2$Ru(IV)=CH-(4-isopropylphenyl) (catalyst F).

Cl_2[P(cyclohexyl)$_3$]$_2$Ru(IV)=CH-(4-tert-butylphenyl) (catalyst G).

Abbreviations:

DCPD: dicyclopentadiene

DSC: differential scanning calorimetry (heating rate 10°C/min)

TGA: thermogravimetric analysis (heating rate 10°C/min)

WL: weight loss of polymer powders in % in the temperature range from room temperature to 300 °C determined by TGA

SWE: swelling in toluene (increase in weight in % after 24h storing in toluene)

REA: reactivity ΔH determined by DSC (in J/g)

T_g: glass transition temperature (°C)

CAT: catalyst in % by weight, based on monomer, e.g. DCPD

n.d.: not determined

RT: room temperature

Examples 1-6:

20 g of DCPD (technical quality, produced by Shell) are degassed for 3 min under vacuum ($3x10^6$ Pa) at 45 °C shortly before the catalyst is added. The catalysts are then added and dissolved. If CH_2Cl_2 is used as solubiliser, the mixture is subsequently degassed again under vacuum and CH_2Cl_2 is removed. The composition is polymerised in a pill glass, curing cycle: 1h at 80 °C, 1h at 100 °C and 2h at 120 °C.

The reactivity (ΔH) and glass transition temperature are determined by DSC. The weight loss is determined by TGA and swelling is determined gravimetrically. The results are summarised in Table 1.

Table 1:

Example	CAT A	CAT B	ΔH	T_g	WL	SWE	Remarks
comparison	0.2	---	n.d.	<RT	15.0	n.d.	soft rubber, smell of DCPD
comparison	0.1	---	187	<RT	n.d.	n.d.	soft rubber, smell of DCPD
comparison	---	0.1	288	39	19.5	94	soft solid, smell of DCPD
comparison	--	0.05	n.d.	<RT	>30	n.d.	incompletely polymerised
comparison	--	0.025	n.d.	<RT	>30	n.d.	incompletely polymerised
1	0.2	0.1	289	124	3.1	97	hard solid, no smell of DCPD
2	0.1	0.1	282	120	2.8	94	hard solid, no smell of DCPD
3	0.15	0.05	302	121	3.6	100	hard solid, no smell of DCPD
4	0.175	0.025	261	109	4.1	99	hard solid, no smell of DCPD
5	0.1	0.05	n.d.	123	3.7	84	hard solid, no smell of DCPD
6	0.05	0.05	n.d.	119	4.4	87	hard solid, no smell of DCPD

Example 7:

Example 1 is repeated, but using catalyst C. The results are summarised in Table 2.

Table 2:

Example	CAT C	CAT B	ΔH	T_g	WL	SWE	Remarks
comparison	up to 0.5	---					no polymerisation
comparison	---	0.1	288	39	19.5	94	soft solid
comparison	--	0.05	n.d.	<RT	>30	n.d.	incompletely polymerised
comparison	--	0.025	n.d.	<RT	>30	n.d.	incompletely polymerised
7	0.15	0.05	n.d.	<20	n.d.	n.d.	soft rubber, strong smell of DCPD

<u>Examples 7 and 8:</u>

Example 1 is repeated, but using catalyst D. The results are summarised in Table 3.

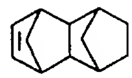
Table 3:

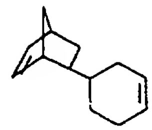
Example	CAT D	CAT B	ΔH	T_g	WL	SWE	Remarks
comparison	up to 0.5	---					no polymerisation
comparison	---	0.1	288	39	19.5	94	soft solid
comparison	--	0.05	n.d.	<RT	>30	n.d.	incompletely polymerised
comparison	--	0.025	n.d.	<RT	>30	n.d.	incompletely polymerised
7	0.1	0.1	286	61	11.1	n.d.	soft solid
8	0.15	0.05	258	28	19.5	n.d.	soft solid

<u>Examples 9-14:</u>

Example 1 is repeated, but using the catalyst and monomers indicated in Table 4. The results are given in Table 4.

Monomers used

α : tetracyclododecene (TD) 

β : cyclohexenylnorbornene (CN) (endo/exo-mixture) 

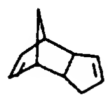
γ : DCPD 

Table 4

Example	Monomer	1. CAT [%]	2. CAT [%]	T_g [°C]	WL [%]	Observations
comparison	α	E; 0.02	-	-	-	not polymerised
comparison	α	F; 0.02	-	< 25	-	yellow rubber
comparison	α	A; 0.15	-	118	18.1	polymerised
comparison	α	A; 0.02	-	130	11.8	polymerised
9	α	E; 0.02	A, 0.15	177	14.7	polymerised
10	α	F; 0.02	A; 0.15	174	13.3	polymerised
comparison	β	E; 0.02	-	<25	-	yellow rubber
comparison	β	F; 0.02	-	<25	-	yellow rubber
comparison	β	A; 0.50	-	96	-	polymerised
comparison	β	A; 0.15	-	79	5.9	polymerised
11	β	E; 0.02	A; 0.15	94	3.1	polymerised
12	β	F; 0.02	A; 0.15	84	4.7	polymerised
comparison	γ	E; 0.05	-	<25	-	yellow rubber
comparison	γ	F; 0.05	-	<25	-	yellow rubber
comparison	γ	A; 0.15	-	<25	-	yellow rubber
13	γ	E; 0.05	A; 0.15	60	7.8	polymerised
14	γ	F; 0.05	A; 0.15	73	8.0	polymerised

Example 15:

A large condenser (paper/Al foil) is predried overnight at 80°C under high vacuum in a desiccator.

A mixture of 1.2 kg of degassed DCPD (technical quality, produced by Shell) is mixed with 2.4 g (0.2 %) of catalyst A and 1.2 g (0.1%) of catalyst G and this mixture is poured to the condenser in a 2 L beaker glass. The mixture is then degassed at room temperature and 0.2 mbar for about 20 minutes and then cured in an oven: 1 hour at 50°C, 1 hour at 60°C, and 1 hour at 70°C. The highly viscous formulation is then postcured for 15 hours at 70°C, giving a solid brown material having good condensing properties.

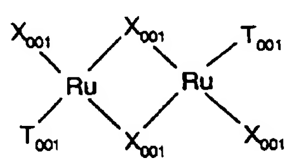
The T_g value determined by DSC is 33°C. The weight loss determined by TGA is 27%.

What is claimed is:

1. A mixture of at least one thermal carbene-free ruthenium catalyst A and at least one thermal ruthenium carbene catalyst B, both of which initiate the ring-opening metathesis polymerisation on their own, said catalysts being present in a weight ratio of A to B from10 :1 to 1:10.

2. A mixture according to claim 1, wherein the ruthenium catalyst A is a compound having one or two ruthenium atoms.

3. A mixture according to claim 2, wherein the carbene-free ruthenium catalyst A is a compound of formula XI



(XI),

wherein X_{001} is Cl, Br or I, preferably Cl, and T_{001} is unsubstituted or C_1-C_6alkyl-substituted C_6-C_{18}arene or C_4-C_{17}heteroarene.

4. A mixture according to claim 1, wherein the ruthenium catalyst A contains a phosphine ligand.

5. A mixture according to claim 4, wherein the ruthenium catalyst A is a divalent-cationic compound containing at least one phosphine ligand and a total of 2 to 5 ligands bonded to the ruthenium atom and which contains acid anions for charge equalisation.

6. A mixture according to claim 4, wherein the phosphine ligand conforms to formulae VII and VIIa

$$PR_{26}R_{27}R_{28} \qquad (VII),$$

$R_{26}R_{27}P\text{-}Z_1\text{-}PR_{26}R_{27}$ (VIIa),

wherein R_{26}, R_{27} and R_{28} are each independently of one another H, C_1-C_{20}alkyl, C_1-C_{20}-alkoxy; C_4-C_{12}cycloalkyl or cycloalkoxy which is unsubstituted or substituted by C_1-C_6alkyl, C_1-C_6haloalkyl or C_1-C_6alkoxy, or C_6-C_{16}aryl or C_6-C_{16}aryloxy which is unsubstituted or substituted by C_1-C_6alkyl, C_1-C_6haloalkyl or C_1-C_6alkoxy, or C_7-C_{16}aralkyl or C_7-C_{16}aralkyloxy which is unsubstituted or substituted by C_1-C_6alkyl, C_1-C_6haloalkyl or C_1-C_6alkoxy; R_{26} and R_{27} together are tetra- or pentamethylene or tetra- or pentamethylenedioxyl, each of which is unsubstituted or substituted by C_1-C_6-alkyl, C_1-C_6haloalkyl or C_1-C_6alkoxy, or tetra- or pentamethylene or tetra- or pentamethylenedioxyl, each of which is unsubstituted or substituted by C_1-C_6alkyl, C_1-C_6haloalkyl or C_1-C_6-alkoxy and condensed with 1 or 2 1,2-phenylene, or tetramethylenedioxyl which is unsubstituted or substituted by C_1-C_6alkyl, C_1-C_6haloalkyl or C_1-C_6alkoxy and condensed in the 1,2- and 3,4-positions with 1,2-phenylene, and R_{28} is as defined above; and
Z_1 is linear or branched, unsubstituted or C_1-C_4alkoxy-substituted C_2-C_{12}alkylene, unsubstituted or C_1-C_4alkyl- or C_1-C_4alkoxy-substituted 1,2- or 1,3-cycloalkylene of 4 to 8 carbon atoms, or unsubstituted or C_1-C_4alkyl- or C_1-C_4alkoxy-substituted 1,2- or 1,3-heterocycloalkylene having 5 or 6 ring members and a hetero atom selected from the O or N group.

7. A mixture according to claim 1, wherein the ruthenium compound A conforms to one of formulae VIII to VIIId

$R_{32}L_1Me^{2+}(Z^{n-})_{2/n}$ (VIII),

$R_{32}L_1L_2Me^{2+}(Z^{n-})_{2/n}$ (VIIIa),

$(R_{32})_2L_1Me^{2+}(Z^{n-})_{2/n}$ (VIIIb),

$(R_{32})_3L_1Me^{2+}(Z^{n-})_{2/n}$ (VIIIc),

$R_{32}(L_1)_2Me^{2+}(Z^{n-})_{2/n}$ (VIIId),

wherein

R_{32} is a phosphine ligand of formula VII or VIIa;

Me is Ru;

n is 1, 2 or 3;

Z is the anion of an inorganic or organic acid;

(a) L_1 is a ligand of group A, L_1 in formula VIId being identical or different, and

(b) L_2 is a ligand of group B.

8. A mixture according to claim 1, wherein the ruthenium compound A conforms to one of formulae IX to IXd

$$(R_{26}R_{27}R_{28}P)L_1Me^{2+}(Z_1^{1-})Z_2^{-1} \quad \text{(IX)},$$

$$(R_{26}R_{27}R_{28}P)_2L_1Me^{2+}(Z_1^{1-})Z_2^{-1} \quad \text{(IXa)},$$

$$(R_{26}R_{27}R_{28}P)L_1L_2Me^{2+}(Z_1^{1-})Z_2^{-1} \quad \text{(IXb)},$$

$$(R_{26}R_{27}R_{28}P)_3L_1Me^{2+}(Z_1^{1-})Z_2^{-1} \quad \text{(IXc)},$$

$$(R_{26}R_{27}R_{28}P)(L_1)_2Me^{2+}(Z_1^{1-})Z_2^{-1} \quad \text{(IXd)},$$

wherein

Me is Ru;

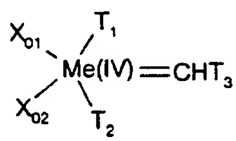
Z_1 and Z_2 are each independently of the other H^-, cyclopentadienyl, Cl^-, Br^-, BF_4^-, PF_6^-, SbF_6^-, AsF_6^-, $CF_3SO_3^-$, C_6H_5-SO_3^-, 4-methyl-C_6H_5-SO_3^-, 3,5-dimethyl-C_6H_5-SO_3^-, 2,4,6-trimethyl-C_6H_5-SO_3^- or 4-CF_3-C_6H_5-SO_3^-;

R_{26}, R_{27} and R_{28} are each independently of one another C_1-C_6alkyl, or cyclopentyl or cyclohexyl or cyclopentyloxy or cyclohexyloxy, each of which is unsubstituted or substituted by 1 to 3 C_1-C_4alkyl, or phenyl or benzyl or phenyloxy or benzyloxy, each of which is unsubstituted or substituted by 1 to 3 C_1-C_4alkyl;

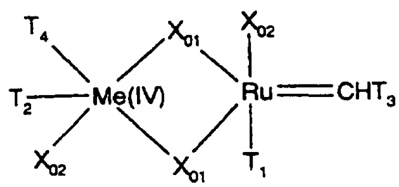
L_1 is C_6-C_{16}arene or C_5-C_{16}heteroarene which is unsubstituted or substituted by 1 to 3 C_1-C_4alkyl, C_1-C_4alkoxy, -OH, -F or Cl, or C_1-C_6alkyl-CN, benzonitrile or benzylnitrile, L_1 in formula IXd being identical or different; and

L_2 is H_2O or C_1-C_6alkanol.

9. A mixture according to claim 1, wherein the ruthenium carbene catalyst B conforms to formula X or Xa or to mixtures of compounds of formulae X and Xa,



(X),



(Xa),

wherein

Me is ruthenium;

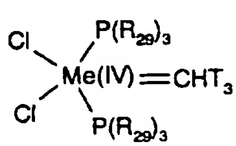
T_1 and T_2 are each independently of the other a tertiary phosphine, or T_1 and T_2 together are a ditertiary diphosphine;

T_3 is H, C_1-C_{12}alkyl; C_3-C_8cycloalkyl, C_3-C_7heterocycloalkyl having one or two hetero atoms selected from the group consisting of -O-, -S- and -N-, C_6-C_{14}aryl, or C_4-C_{15}heteroaryl having one to three hetero atoms selected from the group consisting of -O-, -S- and -N- , which are unsubstituted or substituted by C_1-C_{12}alkyl, C_1-C_{12}haloalkyl, C_1-C_{12}alkoxy, C_6-C_{10}aryl, C_6-C_{10}-aryloxy -NO_2 or halogen;

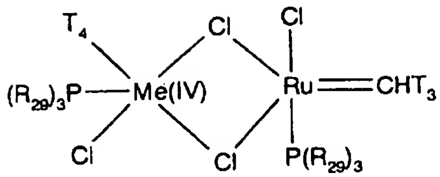
T_4 is C_6-C_{16}arene or C_4-C_{15}heteroarene which is unsubstituted or substituted by 1 to 3 C_1-C_4-alkyl, C_1-C_4haloalkyl, C_1-C_4alkoxy, -OH, F, Cl or Br, and

X_{01} and X_{02} are each independently of the other halogen.

10. A mixture according to claim 1, wherein the ruthenium carbene catalyst B conforms to formulae Xb and Xc



(Xb),



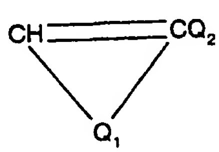
(Xc),

wherein Me is Ru, R_{29} is α-branched C_3-C_8alkyl, C_5-C_8cycloalkyl which is unsubstituted or substituted by C_1-C_4alkyl, C_1-C_4haloalkyl, C_1-C_4alkoxy, halogen or $-NO_2$, or C_6-C_{10}aryl which is unsubstituted or substituted by C_1-C_4alkyl, C_1-C_4haloalkyl, C_1-C_4alkoxy, halogen or $-NO_2$, T_3 is H, C_1-C_6alkyl, C_5-C_8cycloalkyl which is unsubstituted or substituted by C_1-C_4alkyl, C_1-C_4haloalkyl, C_1-C_4alkoxy, halogen or $-NO_2$, or C_6-C_{10}aryl which is unsubstituted or substituted by C_1-C_4alkyl, C_1-C_4haloalkyl, C_1-C_4alkoxy, halogen or $-NO_2$, and T_4 is phenyl or phenyl substituted by 1 to 3 C_1-C_4alkyl.

11. A composition consisting of (a) at least one strained cycloolefin and (b) a catalytically effective amount of a mixture of at least one thermal carbene-free ruthenium catalyst A and at least one thermal ruthenium carbene catalyst B, both of which initiate the ring-opening metathesis polymerisation on their own, said catalysts being present in a weight ratio of A to B from 10:1 to 1:10.

12. A composition according to claim 11, wherein the mixture is present in the composition in an amount from 0.05 to 0.3 % by weight, based on the amount of the cycloolefins present.

13. A composition according to claim 11, wherein the cycloolefin conforms to formula II



(II),

wherein

Q_1 is a radical having at least one carbon atom which, together with the -CH=CQ_2- group, forms an at least 3-membered alicyclic ring which may contain one or more than one hetero atom selected from the group consisting of Si, P, O, N and S; and which is unsubstituted or substituted by halogen, =O, -CN, -NO_2, $R_1R_2R_3Si$-$(O)_u$-, -COOM, -SO_3M, -PO_3M, -$COO(M_1)_{1/2}$, -$SO_3(M_1)_{1/2}$, -$PO_3(M_1)_{1/2}$, C_1-C_{20}alkyl, C_1-C_{20}hydroxyalkyl, C_1-C_{20}haloalkyl, C_1-C_6cyanoalkyl, C_3-C_8cycloalkyl, C_6-C_{16}aryl, C_7-C_{16}aralkyl, C_3-C_6-heterocycloalkyl, C_3-C_{16}heteroaryl, C_4-C_{16}heteroaralkyl or by R_4-X-; or wherein two adjacent carbon atoms, when present, are substituted by -CO-O-CO- or by -CO-NR_5-CO-; or wherein an alicyclic, aromatic or heteroaromatic ring has been fused to adjacent carbon atoms of the alicyclic ring, the former ring being unsubstituted or substituted by halogen, -CN, -NO_2, $R_6R_7R_8Si$-$(O)_u$-, -COOM, -SO_3M, -PO_3M, -$COO(M_1)_{1/2}$, -$SO_3(M_1)_{1/2}$, -$PO_3(M_1)_{1/2}$, C_1-C_{20}alkyl, C_1-C_{20}haloalkyl, C_1-C_{20}hydroxyalkyl, C_1-C_6cyanoalkyl, C_3-C_8cycloalkyl, C_6-C_{16}aryl, C_7-C_{16}aralkyl, C_3-C_6heterocycloalkyl, C_3-C_{16}heteroaryl, C_4-C_{16}heteroaralkyl or by R_{13}-X_1-; X and X_1 are each independently of the other -O-, -S-, -CO-, -SO-, -SO_2-, -O-C(O)-, -C(O)-O-, -C(O)-NR_5-, -NR_{10}-C(O)-, -SO_2-O- or -O-SO_2-; R_1, R_2 and R_3 are each independently of one another C_1-C_{12}alkyl, C_1-C_{12}perfluoroalkyl, phenyl or benzyl; R_4 and R_{13} are each independently of the other C_1-C_{20}alkyl, C_1-C_{20}haloalkyl, C_1-C_{20}hydroxyalkyl, C_3-C_8cycloalkyl, C_6-C_{16}aryl or C_7-C_{16}-aralkyl; R_5 and R_{10} are each independently of the other hydrogen, C_1-C_{12}alkyl, phenyl or benzyl, the alkyl groups in turn being unsubstituted or substituted by C_1-C_{12}alkoxy or by C_3-C_8cycloalkyl; R_6, R_7 and R_8 are each independently of one another C_1-C_{12}alkyl, C_1-C_{12}perfluoroalkyl, phenyl or benzyl; M is an alkali metal and M_1 is an alkaline earth metal; and u is 0 or 1; it being possible for the alicyclic ring formed with Q_1 to contain further non-aromatic double bonds;

Q_2 is hydrogen, C_1-C_{20}alkyl, C_1-C_{20}haloalkyl, C_1-C_{12}alkoxy, halogen, -CN or R_{11}-X_2- , wherein R_{11} is C_1-C_{20}alkyl, C_1-C_{20}haloalkyl, C_1-C_{20}hydroxyalkyl, C_3-C_8cycloalkyl, C_6-C_{16}aryl or C_7-C_{16}aralkyl, and X_2 is -C(O)-O- or -C(O)-NR_{12}- , wherein R_{12} is hydrogen, C_1-C_{12}alkyl, phenyl or benzyl;

the above-mentioned cycloalkyl, heterocycloalkyl, aryl, heteroaryl, aralkyl and heteroaralkyl groups being unsubstituted or substituted by C_1-C_{12}alkyl, C_1-C_{12}alkoxy, -NO_2, -CN or by halogen, and the hetero atoms of the above-mentioned heterocycloalkyl, heteroaryl and heteroaralkyl groups being selected from the group consisting of -O-, -S-, -NR_9- and -N=; and R_9 is hydrogen, C_1-C_{12}alkyl, phenyl or benzyl.

14. A process for the preparation of polymers by ring-opening metathesis polymerisation, which comprises heating a composition according to claim 11.

15. A composition consisting of (a) a support material and (b) a coating of a composition according to claim 1, which is applied to at least one surface.

16. Use of the mixture according to claim 1 as thermal catalyst for the ring-opening metathesis polymerisation of strained cycloolefins.

INTERNATIONAL SEARCH REPORT

Interna   al Application No
PCT/EP 97/01579

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C08G61/08 C08G61/12

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C08G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 96 04289 A (CALIFORNIA INST OF TECHN) 15 February 1996 -----	

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

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"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

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"&" document member of the same patent family

2

Date of the actual completion of the international search	Date of mailing of the international search report
1 August 1997	15.09.97

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Stienon, P

INTERNATIONAL SEARCH REPORT

Information on patent family members

Inter   al Application No
PCT/EP 97/01579

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9604289 A	15-02-96	AU 3272895 A	04-03-96
		CA 2196061 A	15-02-96
		EP 0773948 A	21-05-97